

SnMe_3 groups, we convert the observed frequencies to values of $\sigma^+_{\text{CH}_3} = -0.25$, $\sigma^+_{\text{CH}_2\text{Sn}(\text{C}_6\text{H}_5)_3} = -0.78$, $\sigma^+_{\text{CH}_2\text{SnMe}_3} = -0.93$ by the method previously described.^{3f} From these values we may see that the $-\text{CH}_2\text{Sn}(\text{C}_6\text{H}_5)_3$ group is as activating as a methoxy group^{13a} and the $-\text{CH}_2\text{SnMe}_3$ group is almost as effective as an amino group. By substituting $-\text{SnMe}_3$ for one of the CH_3 hydrogens on toluene the rate of ring acetylation by Friedel-Crafts reaction^{13b} would be accelerated by about 10^6 !¹⁴

But notice what happens when $\text{Sn}(\text{C}_6\text{H}_5)_2$ is substituted for two CH_3 hydrogens in going from VIII to IX. The charge-transfer frequency is slightly increased! A similar substitution of the more activating SnMe_3 group for an α -hydrogen in going from X to XI also results in negligible change. Clearly, when the C-metal bond is in the plane of the aromatic ring, the activation of that ring by the metal group completely disappears. Thus, a factor of $>10^6$ in rate may be removed by rotating the C-metal bond away from the position of overlap with the π system.¹⁵

Having removed the σ - π conjugation effect in structure XI we may now probe the inductive effect by replacing the $-\text{SnMe}_3$ group in XI with other groups, e.g., $-\text{SiMe}_3$, $-\text{HgC}_6\text{H}_{11}$, $-\text{HgCl}$. These substitutions have negligible effect on the CT frequencies indicating that *inductive effects of metallic groups, MR_3 , in the $-\text{CH}_2\text{MR}_n$ group are negligibly small*. It follows from the results with $-\text{HgCl}$ and $\text{HgC}_6\text{H}_{11}$ that the R groups also have *no direct field effect* in this group.

However, the groups R have a *very large indirect inductive effect* on the CH_2MR_n group. This is clearly seen in Figure 1 where the charge-transfer frequencies of benzyl-X and benzylmercuric-X are plotted¹⁶ against σ_X^I . Equations for the two lines are

$$\nu_{\text{TCNE}}^{\text{PhCH}_2\text{X}} (\text{cm}^{-1}) = 4300\sigma_X^I + 24,250 \quad (1)$$

and

$$\nu_{\text{TCNE}}^{\text{PhCH}_2\text{HgX}} (\text{cm}^{-1}) = 11,200\sigma_X^I + 15,700 \quad (2)$$

Both the absolute values of the frequencies for a given X and the slopes¹⁸ of the lines (sensitivity to X) indicate that the *indirect inductive effect* of X, operating through about 3.5 Å, is much greater than the direct-field effect of X operating through only 1.5 Å. This indirect effect can be interpreted as an inductive effect upon M which changes the ability of the $-\text{MR}_n$ group to hyperconjugate.¹⁹

(13) (a) L. M. Stock and H. C. Brown, *Advan. Phys. Org. Chem.*, **1**, 89 (1963); (b) *ibid.*, **1**, 96 (1963).

(14) Even larger accelerations of ring electrophilic substitution reactions were observed with dibenzylmercury.^{3d} Cleavage of C-metal bonds accompanies such ring substitutions.

(15) These results should be compared to similar studies on the (much smaller) effects of C-H hyperconjugation carried out by V. J. Shiner, Jr., *J. Amer. Chem. Soc.*, **82**, 2655 (1960).

(16) The charge-transfer frequencies of $\text{TCNE}-\text{C}_6\text{H}_5\text{CH}_2\text{X}$ have been plotted against σ^* by H. Sakurai¹⁷ who has proposed this as a measure of σ_X^* .

(17) H. Sakurai, private communication.

(18) D. N. Kravtsov and B. A. Faingor (*Izv. Akad. Nauk SSSR, Ser. Khim.*, **2**, 289 (1968)), studied the trinitrobenzene complexes with $p\text{-Me}_2\text{NC}_6\text{H}_4\text{CH}_2\text{X}$ and $p\text{-Me}_2\text{NC}_6\text{H}_4\text{CH}_2\text{HgX}$. They observed that the effect of X in the mercury compound was somewhat less than its effect in $p\text{-Me}_2\text{NC}_6\text{H}_4\text{CH}_2\text{X}$. In this case, most of the charge in the cation radical is on nitrogen.

(19) The fact that $-\text{CH}_2\text{CPh}_3$ or $\text{CH}_2\text{CH}_2\text{OMe}$ is ineffective in σ - π conjugation²⁰ argues against conjugative stabilization of MR_3 of the type $\text{R}_2\text{M}^{\delta+}=\text{R}^{\delta+}$. The absence of delocalization of bonds to the positively charged metal is further indicated by the higher charge-transfer frequency of $\text{PhCH}_2\text{SiPh}_3$ than of $\text{PhCH}_2\text{SiMe}_3$.²⁰

(20) H. J. Berwin, unpublished results.

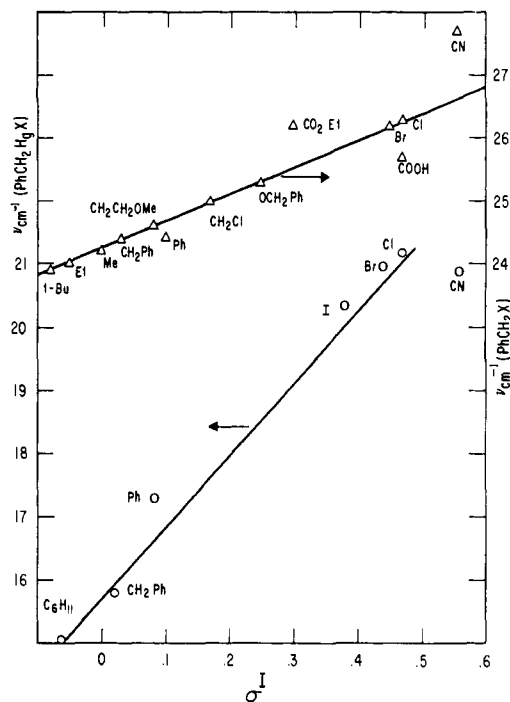
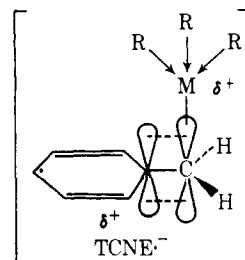


Figure 1. Plots of tetracyanoethylene charge-transfer frequencies of PhCH_2X (Δ) or PhCH_2HgX (\circ) against σ^I . The left ordinate is for the lower plot and the right ordinate for the upper plot. Errors in frequency are about $\pm 300 \text{ cm}^{-1}$.

It thus appears that polarized σ bonds behave in every respect like n electrons on, e.g., nitrogen. The interesting point is that such σ bonds may be chosen



to have conjugating abilities over a range from no conjugation (e.g., $\text{MR}_n = \text{CF}_3$) to conjugation as effective as that of an amino group (e.g., $\text{MR}_n = -\text{HgC}_6\text{H}_{11}$).

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Solvolysis of Bicyclo[3.2.1]octa-2,6-dienyl and Isomeric *p*-Nitrobenzoates^{1,2}

Sir:

Bicyclooctadiene II has been reported by Brown and Occolowicz^{3a} to be more reactive than the monoene I in

(1) Research sponsored by the National Science Foundation.

(2) Reported in part at The Chemical Society 1967 Centenary lecture for the Symposium on "Some Aspects of Organic Reaction Mechanisms," London, England, Oct 10-20, 1967.

(3) (a) J. M. Brown and J. L. Occolowicz, *Chem. Commun.*, 376 (1965); (b) J. M. Brown, *ibid.*, 639 (1967).

Table I. Solvolysis Rate Constants in Aqueous Acetone at 100.0°

ROPNB ^a	10 ⁶ k, sec ⁻¹		<i>exo</i> -ROPNB, 60% acetone rel <i>k</i>
	80%	60%	
<i>exo</i> -V-OPNB	17.6 ± 0.2 ^b	323 ± 16	141
<i>endo</i> -V-OPNB	4.67 ^c		
<i>exo</i> -VI-OPNB	0.276 ± 0.005	2.30 ± 0.12	1.00 (0.60) ^d
<i>exo</i> -VI-OPNB ^e		7.1 ± 0.3	
<i>exo</i> -VI-OPNB/ <i>endo</i> -VI-OPNB		15.3 ± 0.9	
<i>endo</i> -VI-OPNB	0.265 ± 0.003	2.21 ± 0.02	
<i>exo</i> -VII-OPNB	148 ± 2	1640 ± 60	715
<i>endo</i> -VII-OPNB	147 ± 0.3	1660 ± 70	
<i>exo</i> -VIII-OPNB	0.0336	0.309	≥ 0.14

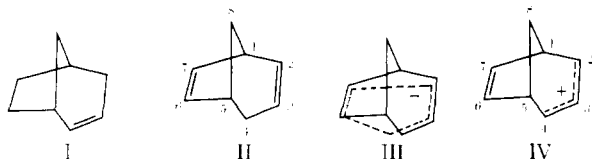
^a ROPNB, 0.0032–0.0076 *M*. ^b *k* for *exo*-V-OPNB at 99.6° is 17.1 × 10⁻⁶ sec⁻¹; H. Goering, private communication. ^c H. Goering, private communication. ^d Corrected for acyl-oxygen cleavage. ^e 0.00445 *M* ROPNB and 0.0141 *M* NaOAc. ^f 0.00431 *M* ROPNB and 0.0437 *M* NaOAc.

Table II. Solvolysis Products at 100.0°

Compd	% acetone	NaOAc, ^a <i>M</i>	% yield, based on recovered products ^b						Total yield, %
			VI-OH		VII-OH		VIII-OH		
			<i>exo</i>	<i>endo</i>	<i>exo</i>	<i>endo</i>	<i>exo</i>	<i>endo</i>	
<i>exo</i> -V-OPNB	60		99.0 (<i>exo</i> -V-OH)						84
<i>exo</i> -VI-OPNB	60	0.00340	75.0	19.0			3.0	3.0	89 ^e
<i>endo</i> -VI-OPNB	60	0.00454	37.5	56.0			3.0	3.0	83 ^e
<i>exo</i> -VII-OPNB	60	0.0445	0.8	0.1	34.2	64.8		0.1	97
<i>endo</i> -VII-OPNB	60	0.0335	0.8	0.1	34.7	63.7		0.1	99
<i>exo</i> -VIII-OPNB	60	0.0101	0.5				94.5		96 ^f
<i>exo</i> -VIII-OTs	80 ^c	0.0055	37.7	14.3			18.4	29.0	84 ^g
<i>endo</i> -VIII-OTs	80 ^c	0.0086	48.9	11.9			32.2	6.2	96 ^g
<i>exo</i> -VIII-OTs	AcOH ^d	0.0216	51.5	16.8			13.4	18.3	60
<i>endo</i> -VIII-OTs	AcOH ^d	0.0195	57.3	15.8			16.1	10.8	66

^a Ester, 0.00302–0.0229 *M*. NaOAc concentration at 50% solvolysis. ^b Product analysis performed by glc using XF-1150 on Chromosorb W packing. ^c 25.0°. ^d Products at 50°; *k* (25°) is 1.3 × 10⁻⁴ sec⁻¹ for *exo*-VIII-OTs and 1.36 × 10⁻⁴ sec⁻¹ for *endo*-VIII-OTs. ^e Plus three unidentified compounds totaling ca. 5–8%. ^f Plus 5% of an unidentified compound. ^g Plus trace amounts of unknowns totaling less than 0.8%.

allylic proton-deuterium exchange by a factor of 10^{4.5} in DMSO-KO-*tert*-Bu at 50°. This increased reactivity of the diene was ascribed to the presence of the additional olefinic group in II, and the possible formulation of the intermediate anion as a bishomocyclopentadienide species III was suggested. HMO calculations do in fact predict a bonding interaction between allylic anion and olefinic systems.^{4a} The interaction is predicted to be quite appreciable even for (β_{27}/β_0) equal to 0.3. The nmr spectrum of the bishomocyclopentadienide anion III has since been reported^{3b,4b} and all features are in accord with the delocalized six-electron bishomoaromatic species with appreciable ring current.



In the carbonium ion analog IV, HMO calculations predict no stabilizing interaction between the allylic cation and the 6,7-olefinic systems. Here, the 6,7-olefinic group makes the cation a four-electron antihomoaromatic bishomocyclopentadienyl species. Therefore, it is of some interest to see the effect of the second olefinic group in solvolyses of the bicyclooctenyl and bicyclooctadienyl *p*-nitrobenzoates. We

(4) (a) S. Winstein, Chemical Society International Symposium on Aromaticity, Sheffield England, July 6–8, 1966; *Chem. Soc. Spec. Publ.*, No. 21, 32 (1967); (b) S. Winstein, M. Ogliaruso, M. Sakai, and J. M. Nicholson, *J. Amer. Chem. Soc.*, **89**, 3656 (1967).

now wish to report the results of such an investigation in this communication.

The dienyl carbinols (VI-OH) were conveniently synthesized by the LiAlH₄ reduction of bicyclo[3.2.1]octa-2,6-dien-4-one⁵ in ethyl ether at -78° which afforded 40% *exo*-VI-OH (mp 45–48°) and 60% *endo*-VI-OH (liquid).⁶ The corresponding *p*-nitrobenzoate esters were prepared in the usual manner; *exo*-VI-OPNB, mp 79–81°, and *endo*-VI-OPNB, mp 72–72.5°. The tetracyclic carbinols (VII-OH) prepared as previously described⁷ were converted to the corresponding *exo*-VII-OPNB, mp 127–129°, and *endo*-VII-OPNB, mp 101–103°, in the usual manner.⁶ The *exo*-VIII-OH, mp 45–47°, was obtained by the LiAlH₄ reduction of *exo*-VIII-OAc available from another investigation.⁸ Chromic acid oxidation of *exo*-VIII-OH to the ketone followed by aluminum isopropoxide reduction in isopropyl alcohol at 100° provided a 45–55% mixture of *exo*-VIII-OH and *endo*-VIII-OH (mp 38–40°).⁶ The corresponding tosylate esters were prepared in the usual manner; *exo*-VIII-OTs, mp 52–53°, and *endo*-VIII-OTs, mp 67–69° dec.⁶

The rates of solvolysis of the alkyl *p*-nitrobenzoates were measured in aqueous acetone. Good first-order kinetics were observed and the infinity titers were

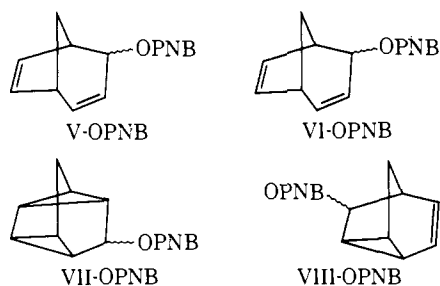
(5) P. K. Freeman and D. G. Kuper, *Chem. Ind. (London)*, 424 (1965).

(6) All new compounds reported gave elemental analyses and spectral data in accord with their assigned structures.

(7) N. A. Le Bel and R. N. Liesemer, *J. Amer. Chem. Soc.*, **87**, 4301 (1965).

(8) J. M. Nickolson, unpublished work.

96.0–97.5% of the theoretical values. The titrimetric rate constants are summarized in Table I.



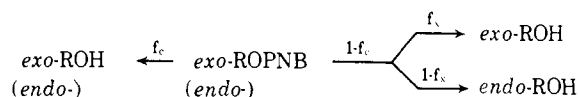
As might be anticipated, the presence of the additional double bond in VI-OPNB is markedly rate retarding. The alkyl-oxygen ionization of the *exo*-bicyclic dienyl VI-OPNB is 235 times slower than the monoene analog. The rate retardation is probably even larger than can be ascribed to the rate-retarding inductive effect of the second olefinic group in line with the anti-homoaromatic designation for the first intermediate cation formed in the solvolysis of the dienyl *p*-nitrobenzoate. Another interesting effect is revealed by comparison of the *exo*:*endo* rate ratios. In the monoene V-OPNB, the ratio is 3.8, possibly reflecting rate retardation in the *endo* epimer due to steric effects of the *endo* hydrogen on C-7. This ratio is reduced to unity in the dienyl VI-OPNB esters.⁹

While the product from the monoenyl *exo*-V-OPNB is 99% *exo*-V-OH,¹⁰ the products from the dienyl VI-OPNB are largely the *exo*- and *endo*-bicyclic dienyl VI-OH mixture together with small amounts of tricyclic alcohols. The results are summarized in Table II. Product analysis for the dienyl VI-OPNB is difficult since even the milder buffers like NaOAc afford a considerable amount of acyl-oxygen cleavage. However, the fraction of solvolysis going by alkyl-oxygen cleavage and the *exo*:*endo*-dienyl product ratio from the carbonium ion reaction were estimated by relating the products from the epimeric esters in the scheme below, where f_c is the fraction of acyl-oxygen cleavage and f_x is the fraction of *exo* product from the carbonium ion intermediate. The two required assumptions are that both epimeric dienyl *p*-nitrobenzoates show the same amount of alkyl-oxygen cleavage and that they both produce the same *exo*:*endo*-dienyl product ratio *via* a common intermediate. Calculations of this type indicate solvolysis in the presence of 0.003–0.0045 *M* NaOAc occurs with 60% alkyl-oxygen and 40% acyl-oxygen cleavage where the alkyl-oxygen cleavage reaction produces 90% dienyl-VI alcohols consisting of a 2:1 *exo*:*endo* product ratio. The amount of acyl-oxygen cleavage agrees reasonably well with the rate enhancement with added NaOAc being due wholly to acyl-oxygen cleavage.

The relative solvolytic reactivities of the isomeric alkyl *p*-nitrobenzoates are in the sequence tetracyclic \gg bicyclic $>$ tricyclic. It is difficult to quantitatively

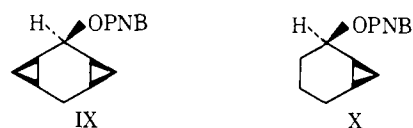
(9) While the absence of steric effects in the *endo*-VI-OPNB could provide an *exo*:*endo* rate ratio of unity, this value may be fortuitous since the marked rate retardations due to the additional olefinic group in the VI esters arise from a blend of factors difficult to resolve and possibly varying in magnitude with structure.

(10) Similarly the acetolysis of *endo*-bicyclo[2.2.2]octen-2-yl tosylate yields the rearranged *exo*-V-OAc, 98.6%, and *endo*-V-OAc, 0.5%, along with 0.4% unrearranged acetate ester (H. L. Goering and D. L. Towns, *J. Amer. Chem. Soc.*, **85**, 2295 (1963)).



assess the relative reactivity for the *exo*-VIII-OPNB since the solvolysis involves mainly acyl-oxygen cleavage. This order is different from that observed in the base-catalyzed proton-deuterium exchange in the corresponding hydrocarbons where the sequence is bicyclic $>$ tricyclic \gg tetracyclic.^{2,4a}

While the tetracyclic VII-OPNB is the most reactive in the series, it is still quite unreactive for a bicyclopropylcarbinyl system. In comparison, VII-OPNB is *ca.* 10^{-4} times less reactive than the similar analog without the 6,7 bond, IX-OPNB,^{11a,b} and only *ca.* twice as reactive as the monocyclopropylcarbinyl X-OPNB.^{11c}



Both epimeric tetracyclic VII-OPNB's yield the same 34.5% *exo* and 64.3% *endo* tetracyclic alcohol mixture amounting to 99% yield along with trace amounts of bicyclic and tricyclic alcohols. The greater portion of *endo*-VII-OH possibly reflects the steric effect of the hydrogen on C-8. The solvolysis products from the tricyclic VIII tosylates are *ca.* 50–60% bicyclic dienyl alcohols and 50–40% tricyclic alcohols where the *endo*-VIII-OTs appears to give more dienyl alcohol. In the dienyl alcohol fraction the *exo* epimer is the greater portion. The nature of the tricyclic alcohol mixtures where *exo*-VIII-OTs yields more *endo*-VIII-OH and *endo*-VIII-OTs yields more *exo*-VIII-OH suggests appreciable direct displacement reaction by solvent.¹² Applying the analogous treatment employed with the bicyclic dienyl products indicates 45% of the tricyclic products are a result of direct solvent displacement and 55% from a common intermediate cation where the *exo*:*endo* ratio for chemical capture is 7:3.

The solvolyses of the isomeric alkyl *p*-nitrobenzoates are accompanied by varying amounts of isomerization where the extent of isomerization is greater with the less reactive esters, thus, *ca.* 1% isomerization with VII-OPNB, *ca.* 10% with VI-OPNB, and *ca.* 70% with VIII-OPNB. However, to the extent that isomerization occurs, only systems VI and VII interchange with negligible leakage to system VIII, suggesting the possible but inefficient intervention of a homopentadienyl cation.¹³

In conclusion, the effect of the second 6,7-olefinic group in the bicyclooctadienyl *p*-nitrobenzoates is rate retarding. Certainly in the solvolysis of the isomeric alkyl *p*-nitrobenzoates a common four-electron anti-homoaromatic bishomocyclopentadienyl

(11) (a) L. Birladeanu, T. Hanafusa, B. Johnson, and S. Winstein, *ibid.*, **88**, 2316 (1966); (b) T. Hanafusa, L. Birladeanu, B. Johnson, and S. Winstein, unpublished results; (c) E. C. Friedrich, unpublished results.

(12) A. F. Diaz, I. Lazdins, and S. Winstein, *J. Amer. Chem. Soc.*, **90**, 1904 (1968).

(13) Calculations by perturbation theory on cation IV suggested that asymmetric interaction with the olefinic group to give a 4,6-homopentadienyl cation is energetically favored, where the charge density is greater on carbons 2, 4, and 7 (D. Blagdon and S. Winstein to be published).

cation species is not achieved analogous to the six-electron bishomocyclopentadienide anion evidenced in the proton-deuterium exchange of bicyclooctadiene II.

(14) Deceased Nov 23, 1969.

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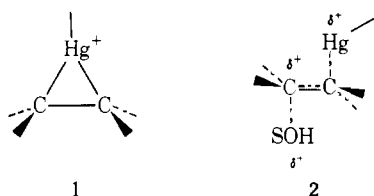
Received July 15, 1970

Oxymercuration of Substituted Cyclohexenes. Evidence for the Fast and Reversible Formation of Mercurinium Ions and the Quantitative Evaluation of Torsional Angle Effects in Transition States¹

Sir:

Since the discovery of the facile addition of mercuric salts to olefins by Hofmann and Sand in 1900,² the solvomercuration of olefins followed by reductive demercuration with sodium borohydride³ has developed into synthetically important methods for the synthesis of alcohols,^{2b,c} ethers,⁴ and amines.^{5,6}

Although numerous investigations have been devoted to the study of the intimate mechanistic details of the solvomercuration reaction, the nature of any intermediate(s) and the transition state is still unresolved in most systems. Mercurinium ions, first proposed by Lucas, Hepner, and Winstein,⁷ have been proposed as intermediates in the solvomercuration of unconjugated, unstrained olefins^{7,8} and allenes.⁹ However, such intermediates have not been directly detected and kinetic studies¹⁰ have not provided unequivocal evidence for or against the intermediacy of mercurinium ions. Fahey¹¹ has pointed out that there was no compelling evidence which demands the intermediacy of mercurinium ions in the solvomercuration of simple unstrained olefins, and suggests that the solvomercuration reaction might well proceed by an A_dE3-type mechanism involving a transition state illustrated as 2.



The only good comparative evidence for the mechanism of a solvomercuration reaction has been pre-

(1) Submitted by J. A. G. in partial fulfillment of the requirements for the Ph.D., University of Notre Dame, Notre Dame, Ind., 1970.

(2) K. A. Hofmann and J. Sand, *Chem. Ber.*, **33**, 1340 (1900).

(3) (a) J. Sand and F. Singer, *ibid.*, **35**, 3170 (1902); (b) F. G. Bordwell and M. L. Douglass, *J. Amer. Chem. Soc.*, **88**, 993 (1966); (c) H. C. Brown and P. Geoghegan, Jr., *ibid.*, **89**, 1522 (1967); D. J. Pasto and J. A. Gontarz, *ibid.*, **91**, 719 (1969).

(4) H. C. Brown and M.-H. Rei, *ibid.*, **91**, 5646 (1969).

(5) A. Latter and J. J. Perić, *Tetrahedron Lett.*, 5165 (1967).

(6) H. C. Brown and K.-T. Liu, *J. Amer. Chem. Soc.*, **91**, 5647 (1969).

(7) H. J. Lucas, F. R. Hepner, and S. Winstein, *ibid.*, **61**, 3102 (1939).

(8) J. E. Herz and E. Gonzalez, *Ciencia (Mexico City)*, **26**, 29 (1968); *Chem. Abstr.*, **69**, 36347g (1968).

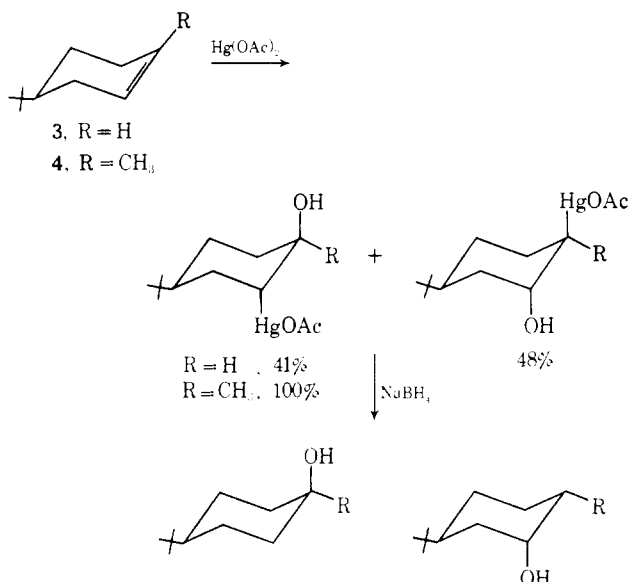
(9) W. L. Waters, W. S. Linn, and M. C. Caserio, *J. Amer. Chem. Soc.*, **90**, 6741 (1968).

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

(11) R. C. Fahey, *Top. Stereochem.*, **3**, 318 (1968).

sented very recently by Brown and Liu.¹² The authors compared the stereochemical course of the reactions of norbornene and 7,7-dimethylnorbornene with mercuric acetate and benzenesulfonyl chloride, the latter proceeding *via* formation of the cyclic episulfonium ion, and concluded that "a cyclic transition state or intermediate, e.g., a mercurinium ion, is probably not involved in this addition process."

In a study in our laboratories designed to determine the nature of steric effects and the structure of intermediates and transition states in electrophilic addition reactions we have studied the stereochemical course of the oxymercuration of a series of substituted cyclohexenes and have compared these results with the results of other addition reactions known to proceed *via* cyclic and noncyclic intermediates and transition states. The kinetically controlled¹³ oxymercuration of 4-*tert*-butylcyclohexene (**3**) and 1-methyl-4-*tert*-butylcyclohexene (**4**) in 50:50 aqueous tetrahydrofuran at 25° produces only diaxial addition products which on reductive demercuration produces only the axial alcohols.¹⁴



The bromination of **3** and **4** with pyridinium hydrobromide perbromide, suggested to proceed *via* a bromonium ion,¹⁵ gives only the diaxial dibromides **5** and **6**, respectively. The methoxybromination of **3** produces only the diaxial products **7** and **8**, whereas the methoxybromination of **4** produces only the diaxial adduct **9**. In contrast, the hydrobromination of **3** and **4** in acetic acid produces both axial and equatorial products consistent with the products expected to be formed in syn and anti A_dE3 additions¹⁶ to **3** and **4**.

The similarity of the results of the oxymercuration, bromination, and methoxybromination of **3** and **4**, and the distinct difference compared to the hydrobromi-

(12) H. C. Brown and K.-T. Liu, *J. Amer. Chem. Soc.*, **92**, 3502 (1970).

(13) Prolonged reaction of the olefins with mercuric acetate leads to the slow formation of equatorial products, the yield of equatorial products slowly increasing to 79% in 10 days at 25°.

(14) Detailed structural assignments of the oxymercuration products and the other electrophilic addition products have been made by nmr studies and glpc comparison with authentic samples and will be discussed in detail in a subsequent article.

(15) J. H. Rolston and K. Yates, *J. Amer. Chem. Soc.*, **91**, 1477 (1969).

(16) D. J. Pasto and G. R. Meyer, unpublished results.