cation species is not achieved analogous to the six-electron bishomocyclopentadienide anion evidenced in the proton–deuterium exchange of bicyclooctadiene 11.

(14) Deceased Nov 23, 1969.

* Author to whom inquiries should be addressed: Department of Chemistry, University of California, La Jolla, California 92037.

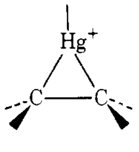
A. F. Diaz,* M. Sakai, S. Winstein[14]
Contribution No. 2615
Department of Chemistry, University of California
Los Angeles, California 90024
Received July 15, 1970

Oxymercuration of Substituted Cyclohexenes. Evidence for the Fast and Reversible Formation of Mercurinium Ions and the Quantitative Evaluation of Torsional Angle Effects in Transition States[1]

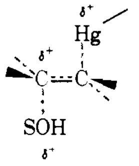
Sir:

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 borohydride[3] 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 studies[10] have not provided unequivocal evidence for or against the intermediacy of mercurinium ions. Fahey[11] 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 AdE3-type mechanism involving a transition state illustrated as **2**.



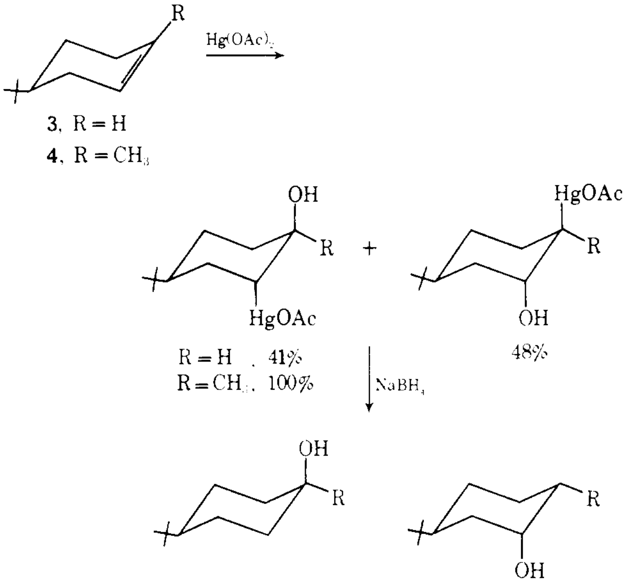
1



2

The only good comparative evidence for the mechanism of a solvomercuration reaction has been presented 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 benzenesulfenyl 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 controlled[13] 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 AdE3 additions[16] 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-

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[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. Perié, *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).

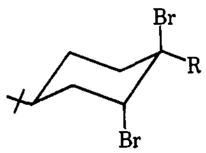
[12] H. C. Brown and K.-T. Liu, *J. Amer. Chem. Soc.*, **92**, 3502 (1970).

[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°.

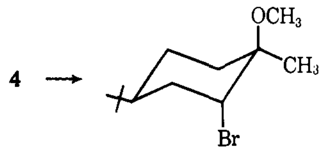
[14] Detailed structural assignments of the oxymercuration products and the other electrophilic addition products have been made by nmr studies and glpc comparison with authentic samples and will be discussed in detail in a subsequent article.

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

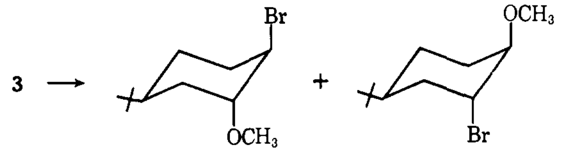
[16] D. J. Pasto and G. R. Meyer, unpublished results.



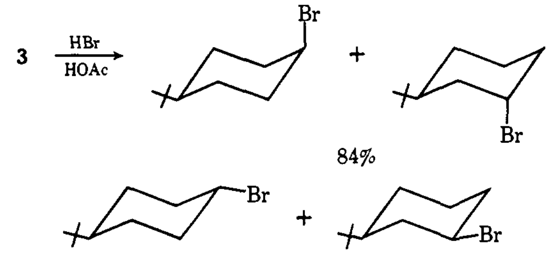
5, R = H
6, R = CH$_3$



9

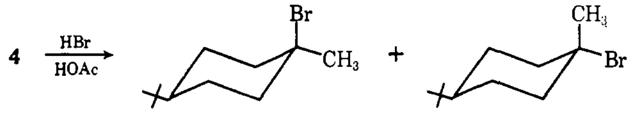


7, 53%   8, 47%



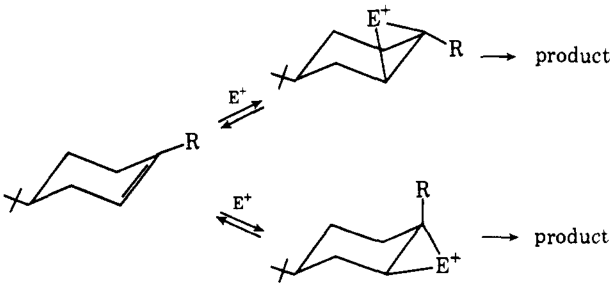
84%

16%

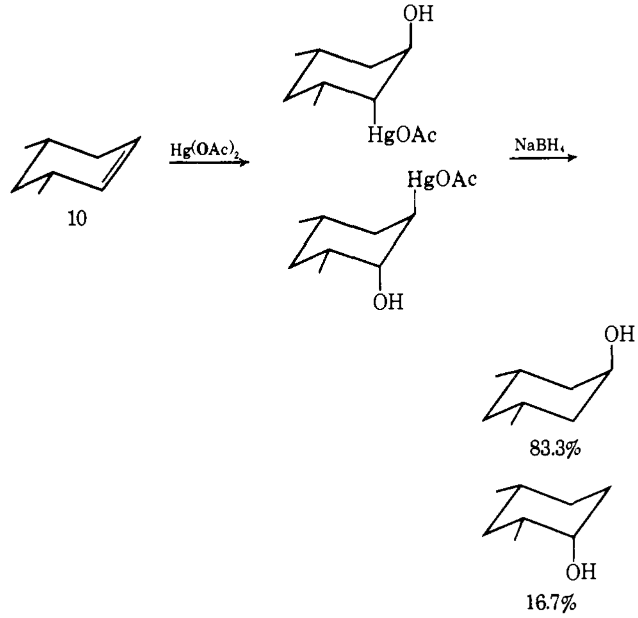


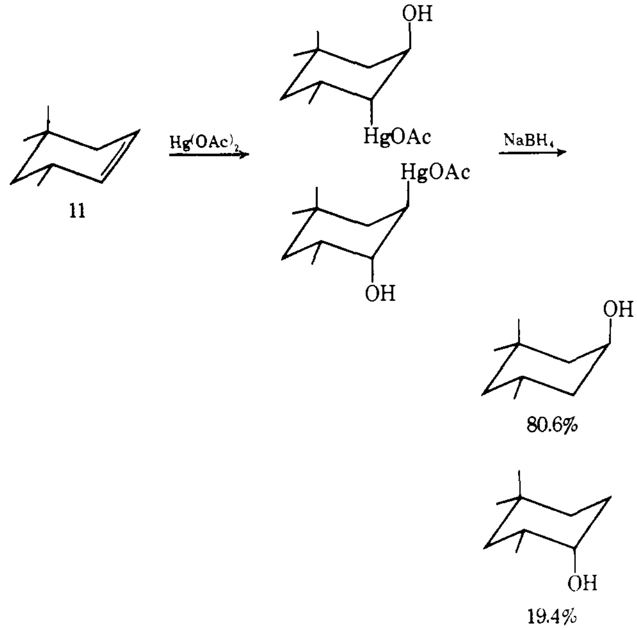
89%   11%

nation results, suggest that the oxymercuration reaction is proceeding *via* formation of a cyclic intermediate (mercurinium ion) which opens to give only trans diaxial products. Comparison of the results derived with **3** and **4** also indicates that mercurinium ion formation must be reversible. With **3** attack by mercuric ion occurs almost to the same extent at both faces of the double bond, whereas the **4** product is derived only from attack at the side trans to the *tert*-butyl group. As previous studies in our laboratories have shown that the 1-methyl group does not influence the direction of attack on the double bond,[17] mercurinium ion formation at both faces of the double bond in **4** must occur; however, the *cis*-mercurinium ion can only open in an anti-Markovnikov or trans diequatorial process. As both of these processes must be of higher energy than the trans diaxial opening process, the *cis*-mercurinium ion must revert to starting materials and reaction proceeds only *via* the *trans*-mercurinium ion.



We have also investigated the steric effects operative in the oxymercuration of substituted cyclohexenes. The results of the oxymercuration of *cis*-2,5-dimethyl- (**10**) and 3,5,5-trimethylcyclohexene (**11**) produce the products shown below. Comparison of the product distribution derived from the two systems shows that the 5-axial methyl of **11** exerts a negligible steric effect. This is in contrast to the hydroboration of **11** in which 84% of the attack by borane occurs trans to the 5-axial methyl group.[17] Keeping in mind that mercurinium ion formation is fast and reversible, and that in the formation of product the solvent molecule must approach the back side of C-1 past the 5-axial methyl group, it is obvious that the steric course of the reaction must be controlled by some steric effect imposed by the 3-methyl group.





In order to further evaluate the nature of the steric effect of the 3-alkyl group we have synthesized a series of *cis*-3-alkyl-5-*tert*-butylcyclohexenes (**12a–d**)[18] and have studied the steric course of the oxymercuration of

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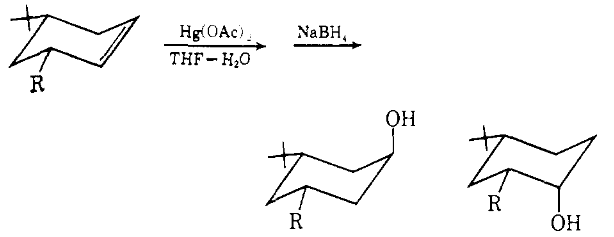
[17] D. J. Pasto and F. M. Klein, *J. Org. Chem.*, 33, 1468 (1968).

[18] Satisfactory analyses have been obtained for all new compounds. The methods of preparation and the physical properties will be reported at a later time.

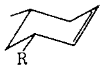
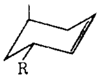
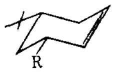
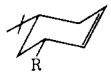
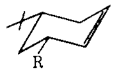
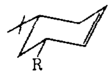
these olefins. The results are given in Scheme I. Changing the nucleophile from water to acetic acid (acetoxymercuration) does not significantly change the steric course of the reaction. The size of the 3-alkyl group has a rather profound effect on the steric course of the reaction. As the products are formed in competitive reactions it is possible to calculate the difference in activation energies ($\Delta\Delta G^{\ddagger}$) of the competitive reaction pathways. These values are given in Table I along with the corresponding *A* values for the alkyl groups.[19] The results are nicely rationalized by invoking torsional angle effects in the transition state for the rate-determining attack by solvent on the mercurinium ion intermediates as illustrated in Scheme II. In the attack by solvent at C_1 in **13** the C_1–H bond moves past the C_6–H_e bond as indicated by the arrow in transition state **14**. In contrast, attack at C_2 in **15** forces the C_2–H bond toward the C_3–R_e bond as indicated in **16**. As the eclipsing strain energy in **16** will be considerably greater than in **14**, reaction *via* **13** will be favored. The results are not consistent with reaction proceeding *via* an AdE3-type transition state. In the AdE3 transition states the C_1–H and C_2–H bonds continuously remain between the C_6–H bonds and the C_3–R_e and C_3–H_a bonds. The present results represent the first quantitative measurement of torsional angle effects.

Scheme I. Results of Oxymercuration of *cis*-3-Alkyl-5-*tert*-butylcyclohexenes

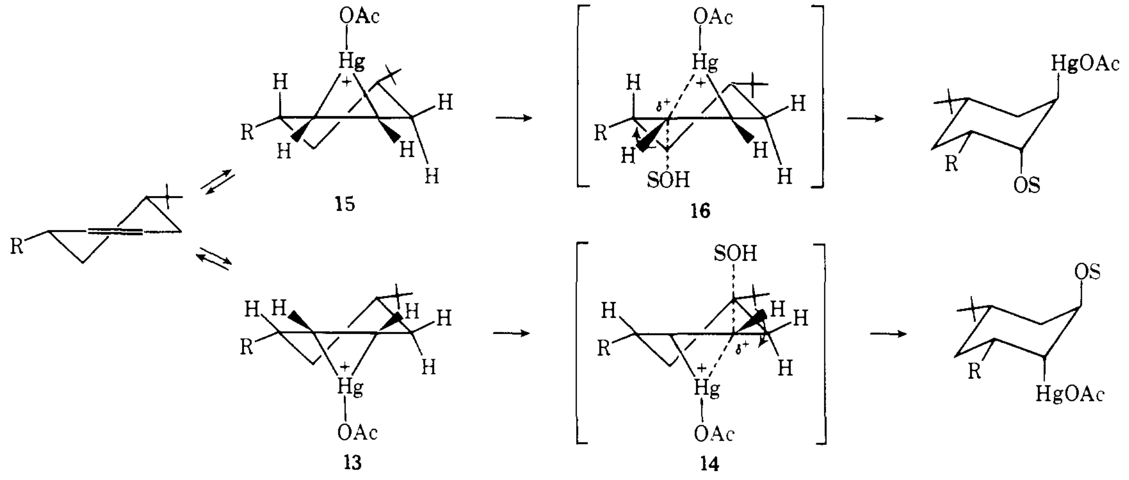


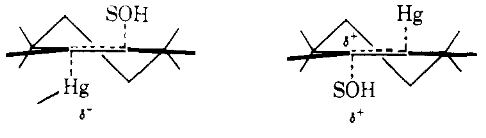
12a, R = $-CH_3$	89.8%	10.2%
b, R = CH_2CH_3	90.5%	9.5%
c, R = $-CH(CH_3)_2$	94.2%	5.8%
d, R = $-C(CH_3)_3$	99.06%	0.94%

Table I. $\Delta\Delta G^{\ddagger}$ Values for Competitive Pathways in the Oxymercuration of 3-Substituted Cyclohexenes

Olefin	R	$\Delta\Delta G^{\ddagger}$	A_R
	CH_3	0.95	1.7
	CH_3	0.85	1.7
	CH_3	1.28	1.7
	C_2H_5	1.33	1.8
	$CH(CH_3)_2$	1.65	2.1
	$C(CH_3)_3$	2.75	~5

Scheme II





Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work (PRF-1225-A1,3), and to the Alfred P. Sloan Foundation for partial support of this work.

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[19] E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience, New York, N. Y., 1966, p 44.

[20] Alfred P. Sloan Fellow, 1967–1969.

* To whom correspondence should be addressed.

Daniel J. Pasto,*[20] John A. Gontarz
Department of Chemistry, University of Notre Dame
Notre Dame, Indiana 46556
Received March 10, 1970

A Mössbauer Study of the Bonding in Ruthenium(II) Compounds

Sir:

Extensive reports of the utilization of Mössbauer spectroscopy in the elucidation of the structure and