

The Stereospecificity of the Alkoxymercuration of Allenes

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Abstract: The ethoxymercuration of optically active 1,2-cyclononadiene with a series of mercuric salts is described. Evidence is presented for the existence of a mercurinium ion intermediate **2** and an allylic carbonium ion **3** which may be formed reversibly from **2**. The stability of **2**, and the relative stereospecificity of the reaction, is shown to be directly related to the mercuric salt utilized in the reaction.

Although a great deal of effort has been expended on the electrophilic addition of mercuric salts to olefins,¹ this reaction has only recently been extended to include reactions with allenes. Gardner and coworkers² have established the mode of addition of mercuric acetate to 1,2-cyclononadiene, 1,2,6-cyclononatriene, and 2,3-pentadiene in ethanol, while Waters and Kiefer³ have described the reaction of allene and its five methyl-substituted derivatives with mercuric acetate in methanol. These authors have presented evidence for the existence of a σ -bridged mercurinium ion intermediate in these reactions. Their results have been corroborated by Waters and Caserio⁴ who have reported that the addition of mercuric acetate to optically active 2,3-pentadiene in methanol proceeds by a *trans* addition affording optically active products.

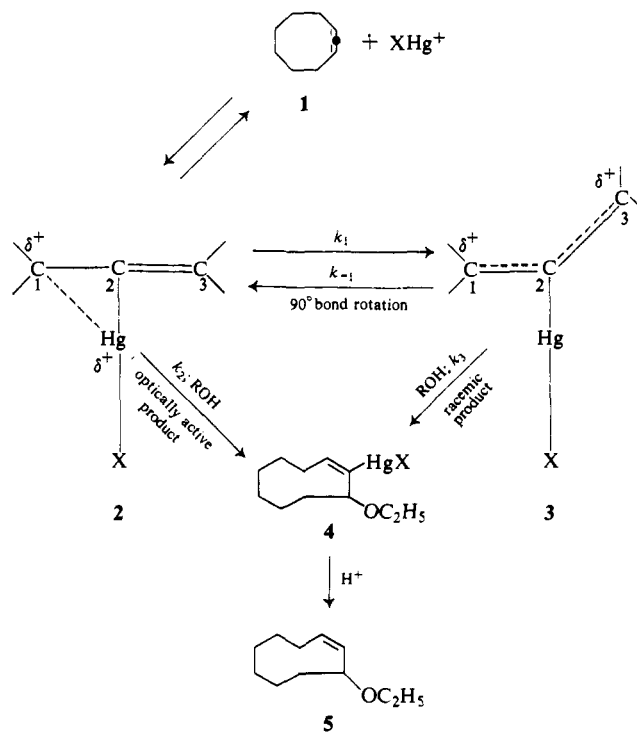
Bridged mercurinium ions⁵ are fashionable for describing the intermediates in the oxymercuration of olefins and recently the observation by nmr of this ion has been claimed.^{6,7} Kinetic evidence suggests that those intermediates which bear an unsaturated substituent possess some carbonium ion character and are resonance stabilized.⁸

The oxymercuration of an optically active allene should provide a rigorous test for the existence of mercurinium ion intermediates bearing unsaturated substituents. The orbitals involved in the formation of the π complex are orthogonal to the plane described by the p orbitals of the adjacent double bond. There is a considerable driving force to form a planar resonance stabilized allylic carbonium ion,⁹ **3**, by a 90° rotation about the carbon-carbon

bond of **2**. The relative amounts of product obtained from **2** and **3** in the oxymercuration of an allene should depend on the nature of the electrophile, as well as the nature and concentration of the nucleophile. Our results on the reaction of optically active 1,2-cyclononadiene with a series of mercuric salts is the subject of this paper.

Results and Discussion

One of the unique features of 1,2-cyclononadiene is that its double bonds appear to be more readily accessible to electrophilic attack from the outside of the ring.¹⁰ This mode of addition affords the *cis* adduct. Our experimental results support this suggestion since the isolated



(1) (a) J. Chatt, *Chem. Rev.*, **48**, 7 (1951); (b) N. S. Zefirov, *Russ. Chem. Rev.*, **34**, 527 (1965); (c) W. Kitching, *Organometal. Chem. Rev.*, **3**, 61 (1968).

(2) R. K. Sharma, B. A. Shoulders, and P. D. Gardner, *J. Org. Chem.*, **32**, 241 (1967).

(3) W. L. Waters and E. F. Kiefer, *J. Amer. Chem. Soc.*, **89**, 6261 (1967).

(4) W. L. Waters and M. C. Caserio, Abstracts, 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967, Abstract S-157; W. L. Waters, W. S. Linn, and M. C. Caserio, *J. Amer. Chem. Soc.*, **90**, 6741 (1968).

(5) (a) H. J. Lucas, F. R. Hepner, and S. Winstein, *J. Amer. Chem. Soc.*, **61**, 3102 (1939); (b) M. M. Kreevoy, G. Stokker, R. A. Kretchner, and A. K. Ahmed, *J. Org. Chem.*, **28**, 3184 (1963); (c) K. Ichikawa, N. Nishimura, and S. Takayama, *ibid.*, **30**, 1593 (1965).

(6) (a) V. I. Sokolov, Y. A. Ustynuk, and O. A. Reutov, *Dokl. Akad. Nauk SSSR*, **173**, 1103 (1967); (b) Y. Saito and M. Matsuo, *Chem. Commun.*, 961 (1967).

(7) W. Kitching, A. J. Smith, and P. R. Wells, *ibid.*, 370 (1968), are in disagreement with the interpretation presented in ref 6b.

(8) L. L. Schaleger, M. A. Turner, T. C. Chamberlin, and M. M. Kreevoy, *J. Org. Chem.*, **27**, 3421 (1962).

(9) (a) The energy available to an allylic radical was estimated to be 12.6 ± 1.0 kcal/mol: K. W. Egger, D. M. Golden, and S. W. Benson, *J. Amer. Chem. Soc.*, **86**, 5420 (1964). (b) Values of 12–25 kcal/mol have been assigned to the resonance energy of an allylic system. For a summary see W. von E. Doering and J. C. Gilbert, *Tetrahedron Suppl.*, **7**, 397 (1966).

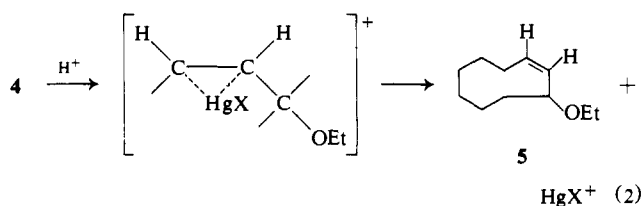
(10) (a) Although molecular models suggest that the molecule may assume a conformation where attack by XHg^+ from within the ring is sterically feasible, examination of the multiple conformations that are possible suggests that this approach is more sterically hindered. Since the double bond is in equilibrium^{10,11} with the mercurinium ion such a hindered transition state is energetically unfavorable and we feel that the *cis* adduct should be formed preferentially. Moreover, the formation of the thermodynamically less stable *trans* adduct involves a transition state with a bulky substituent in the center of an already crowded medium ring. (b) With 1,2-cyclotridecadiene alkoxymercuration afforded the more thermodynamically stable *trans* adduct: R. D. Bach, *Tetrahedron Lett.*, 5841 (1968).

(11) J. Halpern and H. B. Tinker, *J. Amer. Chem. Soc.*, **89**, 6427 (1967).

products from this reaction all contained a *cis* double bond. Evidence for the formation of a trace of the *trans* adduct was observed in one instance (see Experimental Section).^{10b} Without exception solvolysis of intermediates **2** and **3** occurred at C₁ affording an allylic ether (eq 1).

At least two factors, the covalency of the Hg–X bond, and the acidity of the reaction medium as a result of the ionization of HgX₂, determine the fate of the organomercury compounds obtained by the reaction of **1** with mercuric salts. When **1** was treated with mercuric acetate in ethanol solution the product of the reaction was 2-acetoxymethyl-3-ethoxycyclononene (**4a**). However, when the reaction was carried out in the presence of boron trifluoride etherate the reaction medium was sufficiently acidic that acid cleavage of **4a** resulted *in situ* and 3-ethoxycyclononene (**5**) was isolated in high yield. Analysis of the reaction mixture by vpc indicated that greater than 98% of the diene **1** had been consumed providing a useful synthetic modification of this reaction.

Ethoxymercuration reactions of **1** with mercuric perchlorate, mercuric sulfate, mercuric nitrate, and mercuric oxide¹² also resulted in the isolation of **5** *via* the *in situ* acidolysis reaction (eq 2).¹³



A ligand exchange reaction of **4a** with an excess of chloride ion gave 2-chloromercuri-3-ethoxycyclononene (**4b**). The covalent chloromercuri derivative was stable to BF₃ and to dilute hydrochloric acid in ethanol solution; neither acidolysis nor deoxymercuration was observed. As anticipated on the basis of these results and previous work,² the reaction of **1** with mercuric chloride afforded **4b**. The BF₃-catalyzed addition of mercuric fluoride to **1** also gave **4b** after the initially formed fluoromercuri derivative was treated with an excess of chloride ion.

Ethylmercuric acetate, in the presence of boron trifluoride etherate, catalyzed the addition of ethanol to **1**. Best yields were obtained when a stoichiometric amount of the mercury compound was employed. The *in situ* acidolysis of the initially formed product, 2-ethylmercuri-3-ethoxycyclononene,¹⁴ resulted in the isolation of **5**. The oxymercuration reaction did not take place in the absence of BF₃.

The BF₃-catalyzed addition of phenylmercuric acetate to **1** proceeded in a similar fashion affording the allylic ether **5** *via* the acid-cleavage reaction of the intermediate

(12) Mercuric oxide–boron trifluoride etherate has been shown to be an effective catalyst (5 mol %) for the addition of alcohols to 1,3-disubstituted allenes.^{10b}

(13) For a discussion of the mechanism of the acidolysis reaction of vinyl halides see: M. M. Kreevoy and R. A. Kretschmer, *J. Amer. Chem. Soc.*, **86**, 2435 (1964); M. M. Kreevoy and R. A. Landholm, *Int. J. Chem. Kinetics*, in press.

(14) The organomercury compound was not isolated. Its intermediacy is suggested by consideration of the over-all mechanism of the reaction and by analogy to the addition of mercuric acetate to **1** in the presence of BF₃.

phenylmercuri derivative¹⁴ of **1**. The reaction of phenylmercuric acetate with **1** may also be catalyzed by perchloric acid and by fluoroboric acid. The acid catalysis in these reactions suggests an acid–base interaction leading to a more reactive organomercury species (eq 3). To our knowledge these reactions represent the first uses of an alkyl or aryl mercury salt in an oxymercuration reaction.



The formation of optically active 3-ethoxycyclononene (**5**) in this reaction definitely precludes the free carbonium ion **3** as being the sole precursor to **5**. The results, summarized in Table I, provide convincing evidence for the intermediacy of the mercurinium ion **2**. In addition, the relative stereospecificity of this reaction, and consequently the extent of the formation of **3**, is shown to be directly related to the nature of the mercuric salt utilized.

Table I. Reaction of Ethanol with Optically Active 1,2-Cyclononadiene^a

Mercuric salt	Catalyst	Isolated yield of 3-ethoxycyclononene ^b	[α] ^{25D} , deg
C ₂ H ₅ HgOAc ^d	BF ₃	85	+15.3 ^c
C ₆ H ₅ HgOAc ^d	BF ₃	42	+13.6
Hg(OAc) ₂ ^e			+12.4
Hg(OAc) ₂	BF ₃	67	+12.6
Hg(ClO ₄) ₂ ·9H ₂ O	BF ₃	82	+12.1
HgO	BF ₃	73	+11.1
HgSO ₄	BF ₃	72	+10.4
Hg(NO ₃) ₂ ^f		51	+9.9
Hg(NO ₃) ₂	BF ₃	70	+9.9
HgCl ₂ Hg(OAc) ₂ ^{g,h}			+6.2
HgF ₂ ^g	BF ₃		+1.4
HgCl ₂ ^g			+0.1–0.2

^a The 1,2-cyclononadiene used in these experiments had [α]^{25D} –81.8° (c 2.28, methylene chloride). ^b In some cases the yield may be higher due to material loss during isolation. ^c Rotations were measured in methylene chloride solution and the values reported are an average of two experiments that agree within 0.3°. ^d No reaction took place in the absence of boron trifluoride etherate. ^e The initial product of this reaction was 2-acetoxymethyl-3-ethoxycyclononene which was converted to 3-ethoxycyclononene by reduction with sodium in liquid ammonia. However, when a catalytic amount of boron trifluoride etherate was employed, the product was **5**. ^f With mercuric salts that form more strongly acidic solutions boron trifluoride etherate catalysis was not necessary. ^g The initial product isolated was the 3-ethoxy halomercuri derivative which was subsequently converted to 3-ethoxycyclononene. ^h The ratio of HgCl₂ to Hg(OAc)₂ to 1,2-cyclononadiene was 0.5:0.5:1.0.

Inspection of these data reveals that ethylmercuric acetate affords **5** with the highest degree of stereospecificity. As the carbon atom of the ligand was varied from sp³ to the more electronegative sp² carbon atom (PhHg⁺), direct interaction of the aromatic ring and the mercury was possible, and the relative stereospecificity of the reaction decreased. Since **2** is a complex of one of the mutually orthogonal double bonds of the allene with XHg⁺, the distribution of positive charge on the three atoms¹⁵ of the mercurinium ion should respond to this change in structure. In general, attaching a more electronegative atom to the mercury atom in the transition state should increase the carbonium character at C₁, destabilize

(15) The schematic representation of **2** merely implies that positive charge at C₁ is greater than that at C₂ since exclusive cleavage of the C₁–Hg bond was observed.

2, and enhance the formation of the resonance stabilized allylic carbonium ion **3**. This hypothesis is supported by the fact that the five oxygen-bearing ligands lead to a decrease in the stereospecificity of the reaction.

This trend in decreasing the C₁-Hg bond strength of **2** was seen to continue when FHg⁺ was the attacking electrophile, but ClHg⁺ appears to be out of order. Strictly on the basis of the electronegativity of the ligand, ClHg⁺ should form a more stable mercurinium ion under these conditions than the more electronegative oxygen-substituted electrophiles (e.g., ClO₄Hg⁺). However, as a second-row element, it is conceivable that the inductive effect of the chloride ligand may be enhanced by the ability of mercury to π bond to empty chlorine orbitals and further destabilize **2**. This suggestion is not supported by extended Hückel calculations, *vide infra*, which indicated that little d-orbital participation is involved in the mercury-chlorine bond. An alternate explanation for this trend may lie in the varying ability of the ligands to stabilize the carbonium ion **3**, thus affecting the partition between **2** and **3**.

The lack of reactivity of HgCl₂ toward olefins¹ could be due to its low dissociation constant or to the formation of an unstable chloromercurinium ion. An attempt to generate ClHg⁺, *in situ*, from ClHgOAc by the ligand exchange reaction of HgCl₂ and Hg(OAc)₂ in ethanol solution, was apparently not successful. The allyl ether **5**, obtained by reduction² of 2-chloromercuri-3-ethoxycyclohexene (**4b**), had $[\alpha]_D +6.1^\circ$. This indicates that the two mercuric salts either reacted independently, or that ligand exchange occurred affording a finite concentration of the acetoxymercurinium ion which reacts faster with alcohol than the chloro derivative affording some optically active **4a**. However, a much better yield of **4b** was obtained by this procedure.

Explicit in the mechanism described by eq 1 is the reversible formation of carbonium ion **3** from **1**, and the irreversible formation of **4** from either **2** or **3**. By analogy to oxymercuration reactions with olefins, the equilibrium between **1** and **2** is well established.^{10,11} The reversible formation of **3** was demonstrated by stopping the reaction short of completion and examining the optical purity of the unreacted allene. The unreacted diene **1** recovered from the reaction with mercuric chloride had racemized approximately 57%, while the product **5**, isolated after reduction of **4b**, had essentially the same rotation (+0.1–0.2°) as **5** isolated after a reaction time of 14 hr. This suggests that in all cases described here, the rate of the combined reactions leading to products (*i.e.*, $k_2 + k_3$) is always greater than the reverse process (k_{-1}) affording the starting material **1** after demercuration. In a separate experiment the allene was shown to be optically stable in an ethanolic solution of **4b**. The most reasonable mode of racemization of **1** is the reversible formation of the planar carbonium ion **3** followed by demercuration of **2** leading to racemic **1**. This, of course, provides a pathway to racemic **5**.

When the aforementioned experiment was carried out with mercuric acetate, which yields a relatively stable mercurinium ion, the unreacted **1** had retained 92% of its optical activity. The optical purity of the 3-ethoxycyclohexene, obtained by the reduction of **4a**, was independent of reaction time, suggesting the irreversible formation of **4**, and had the same rotation as **5** obtained by the BF₃-catalyzed *in situ* acidolysis of **4a**. A measurable extent

of racemization of unreacted **1** could not be detected when this diene was allowed to react with ethylmercuric acetate and boron trifluoride etherate. This result suggests that EtHg⁺ affords a mercurinium ion of exceptionally low energy and that, indeed, if **3** is formed it does not revert back to **2**.

A series of control experiments established that the varying optical purity of **5** was not an artifact of the reaction conditions or isolation procedures. The diene **1** was not appreciably (<9%) racemized in ethanol solution by boron trifluoride etherate even after stirring 14 hr at room temperature. The allyl ether **5** was shown to be optically stable to the sodium-ammonia reduction conditions and was not racemized by mercuric chloride or by perchloric acid and boron trifluoride etherate in ethanol solution. The optical and chemical stability of **4b** in the presence of mercuric chloride further establishes the irreversibility of the solvolysis reaction yielding **4b**, since it was under these conditions that the greatest extent of racemization of **1** was observed, and the lowest optical activity of **5** resulted.

The above observations are in agreement with the proposed relative stability of the mercurinium ion intermediates and supports the contention that products may arise in part *via* solvolysis of the carbonium ion **3**. Consistent with these results is the suggestion that **3** may be formed reversibly from **1** and that the formation of **4** is irreversible.

In contrast to the conclusions reached by Waters and Kiefer³ the mercurinium ion derived from mercuric acetate is *not* completely prevented from undergoing a 90° C-C bond rotation affording the resonance-stabilized carbonium ion. This provides an alternate pathway for the addition of mercuric acetate to methyl-substituted allenes in methanol since these reactions could proceed in part *via* an allylic carbonium ion intermediate. Our results indicate that the relative stereospecificity of this reaction with mercuric acetate is approximately 80% of that with ethylmercuric acetate and at this point there is no evidence that the latter reaction goes with complete retention of optical activity. However, the lack of reversibility in this reaction could be interpreted in terms of a highly stereospecific reaction.

Our data clearly imply a finite value for k_1 but do not allow us to establish the relative magnitude of k_2 and k_3 . We have demonstrated that X has a marked effect on the ratio of k_1 to k_2 , since when X = Cl the product of the reaction is very nearly racemic. It is in fact this ratio which determines the stereochemical fate of this reaction. The ratio of racemic to optically active product does not depend on the population of optically active **2** relative to **3** and racemic **2**. The stereospecificity of the reaction is dependent on the difference in free energy of the two transition states (ΔF^\ddagger) for **2** leading to **3** (k_1) and to optically active **4** (k_2), and is independent of the energy of the mercurinium ion **2**.¹⁶ Moreover, the relative thermodynamic stability of **2** and **3** should be reflected in the

(16) This concept is valid even though dynamic equilibrium between **2** and **3** is never attained.¹⁷ Conversion of **2** to **3** ultimately results in racemic product since the process of racemization does not depend solely on the solvolysis of **3**. However, if rapid equilibrium has not been attained, and if racemic material was formed only from **3**, then the stereospecificity of the reaction would be dependent on the relative concentration of **2** and **3** and not on ΔF^\ddagger .

(17) D. Y. Curtin, *Record Chem. Progr.*, **15**, 111 (1954); D. Y. Curtin and M. C. Crew, *J. Amer. Chem. Soc.*, **77**, 354 (1955).

Table II. Charge Distributions on **6**

Compd	Charge on H	Charge on C	Charge on Hg	Charge on X
6a	0.089 0.089	0.410	0.803	-0.392
6b	0.101 0.101	0.519	1.090	-0.811
6c	0.089 0.089	0.402	0.692	-0.251 -0.007 -0.007 -0.006
6d	0.095 0.095	0.469	0.946	-0.949 0.342

difference between the free energies of these transition states. Optically inactive product could result either from attack of solvent on the planar carbonium ion **3** or by reversion of **3** to **2**, followed by solvolysis of racemic **2**.¹⁸ Reversion of **3** to **2** is a unimolecular process and could compete favorably with solvolysis of **3**, a bimolecular reaction. It may also be concluded from the pronounced effect of the counterion, X, on the stereospecificity of this reaction, that even with the most ionic mercuric salts (e.g., ClO₄⁻) X is bonded to the mercury (or exists as an intimate ion pair) in the transition state of this reaction in ethanol solvent. This suggestion is not inconsistent with a recent study by Halpern and Tinker on the kinetics of the hydroxymercuration of olefins since their work was carried out in dilute aqueous medium where ionic aggregates are less likely to form.¹¹

A question which is pertinent to the relative stability of **2** and **3** is the electronic effect of -HgX on the stabilization of an allylic carbonium ion relative to hydrogen. Intuitively it would appear that the mercury substituent should be effective in dispersing the positive charge on the cation resulting in a lowering of the energy of the system. Moreover, since we have observed X to have a marked effect on the stability of **2**, we feel that it should also influence the stability of the cation **3**.

In an effort to ascertain the nature of the bonding between -HgX and a cation, extended Hückel calculations as developed by Hoffman¹⁹ were carried out on the simplified system **6**. The coulomb integrals, H_{ii} , were set equal to the valence orbital ionization potentials²⁰ for the particular orbital involved. The valence orbital ionization potential (3d) for the 3s²2p⁴3d¹ configuration of chlorine was estimated to be 2.0 eV by interpolating between averaged states (3d¹) for sulfur and argon given by

(18) As the positive charge at C₁ increases, we cannot preclude the possibility that some fraction of the loss of stereospecificity is due to solvolysis of **2**, from the front and rear, leading to racemic **4**. However, this is still a reflection of the relative stability of the mercurinium ion intermediates.

(19) R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, **36**, 2179 (1962); R. Hoffmann, *ibid.*, **39**, 1397 (1963).

(20) (a) H. Basch, A. Viste, and H. B. Gray, *ibid.*, **44**, 10 (1966); H. Basch, Ph.D. Thesis, Columbia University, 1966. (b) The charge distribution on **6** was not significantly different when valence state ionization potentials were used: J. Hinze and H. H. Jaffé, *J. Amer. Chem. Soc.*, **84**, 540 (1962).

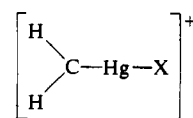
(21) C. E. Moore, "Atomic Energy Levels," U. S. National Bureau of Standards Circular 467, U. S. Government Printing Office, Washington, D. C., 1949 and 1952.

(22) Bond angles and distances were taken from: L. E. Sutton, Ed., "Tables of Interatomic Distances and Configurations in Molecules and Ions," Special Publication No. 11, The Chemical Society, London, 1958. The Hg-O and Hg-F bond distances were estimated to be 2.03 Å.

Moore.^{21,22} Similarly, the VOIP's for the mercury atom were calculated to be 10.44, 5.00, and 15.66 for the 6s, 6p, and 5d orbitals, respectively. The resonance integrals, H_{ij} , were evaluated by using the Wolfsberg-Helmholz expression ($K = 1.75$)²³ for both σ and π interactions. The overlap integrals, S_{ij} , were calculated by adjusting the Slater exponents to give an approximate match to calculated SCF overlap integrals.²⁴ Charges were iterated to self-consistency using a charge sensitivity factor (CONCH(I) = 2.0) for all atoms as in eq 4 where q is the charge on atom I.

$$H_{ii} = H_{ii}^0 - \text{CONCH(I)}q(\text{I}) \quad (4)$$

Our primary interest in these calculations at this time is the charge distribution on the cation **6**. Examination of the data in Table II shows methyl and chlorine to be quite effective in dispersing the positive charge on the carbonium ion. The principle bonding mode in all four cations appears to be σ in nature with little involvement of the d orbitals of mercury. As anticipated, however, on the basis of a covalent mercury chlorine bond there is considerably more p-p π bonding in **6a** than in **6b**, **6c**, or **6d**.



- 6a**, X = Cl
6b, X = F
6c, X = CH₃
6d, X = OH (110°)

Of particular interest is the absence of substantial bonding between the 5d orbitals on mercury and the 3d orbitals of chlorine. The relatively high negative charge on fluorine in **6b** is in agreement with the ionic nature of the mercury-fluorine bond and is consistent with the idea of a highly electronegative ligand increasing the positive charge on mercury and destabilizing the mercurinium ion **2**. Likewise the established covalent nature of the mercury-carbon bond is reflected in the relatively small negative charge on the methyl group of **6c**. The relative overlap populations for the -HgX bond in **6a-6d** were 0.53, 0.19, 0.59, and 0.37, respectively, while the relative overlap populations for the CH₂-Hg bond were 0.63, 0.66, 0.60, and 0.64.

Although caution must be exercised in extrapolating calculations on **6** to the more complex allyl compound **3**, the results at least support the above suggestion that the chloro ligand may be better capable of stabilizing the allyl cation **3** than its corresponding mercurinium **2**. In order to be consistent with our experimental results it may be inferred that the ethylmercurinium **3** is of lower energy than the chloromercurinium ion since these calculations indicate that the two allyl carbonium ions **3** would be of comparable stability. However, any explanation for the high optical purity of **5** obtained *via* the ethylmercurinium ion, and the failure to observe any racemization of **1** during this process, must include the difference in the free energy of the transition states for the two processes.

(23) M. Wolfsberg and L. Helmholz, *J. Chem. Phys.*, **20**, 837 (1952).

(24) F. A. Cotton and C. B. Harris, *Inorg. Chem.*, **6**, 369 (1967); D. G. Carroll and S. P. McGlynn, *ibid.*, **7**, 1285 (1968); H. Basch, Ph.D. Thesis, Columbia University, 1966; E. Clementi, Tables of Atomic Functions, Supplement to paper in *IBM J. Res. Develop.*, **9**, 2 (1965).

The above EH calculations lend credence to the suggestion that the allylic carbonium ion **3** is stabilized by dispersal of charge by the mercury substituent. Since a reliable estimate of the resonance energy of an allylic radical is ~ 12 kcal/mol, it seems reasonable to suggest that the stabilization energy of **3** could be as high as 12 kcal/mol.²⁵ Our experimental results indicate that **2** and **3** are of comparable energy and in fact the ethylmercurinium ion may be of lower energy than **3**. Alternatively it may be argued that when X = Cl a lowering of the energy of **3** relative to **2** results. It may, therefore, be suggested that a semiquantitative lower limit of approximately ~ 12 kcal/mol may be placed on the stability derived from a stable mercurinium ion that does not rearrange to the allylic carbonium ion **3**. Admittedly, if some condition prevails which prevents or slows the formation of **3**, e.g., a high energy barrier to rotation through 90° , our observations will not necessarily reflect the relative stabilities of the intermediates **2** and **3**. However, the barrier to rotation of a carbon-carbon bond is usually only on the order of 1-3 kcal/mol.²⁷ An additional factor involved during the transformation of **2** to **3** is the increase in the energy of **2** as the charge on C₁ develops. Due to the orthogonality of the empty p orbital of the incipient carbonium ion to the adjacent double bond, allylic resonance stabilization cannot occur. However, it is possible that along the reaction coordinate the positive charge may be stabilized by properly oriented orbitals on mercury. Although we cannot ascertain the difference in energy between **2** and **3**, the equilibrium constant, which is quite sensitive to substituent effects, cannot differ substantially from unity since there does not appear to be an insurmountable energy barrier in this process. This is in accord with our experimental results since **3** may be formed reversibly from **2** and readily regenerate the starting diene **1**.

Previous investigators have proposed a variety of reaction intermediates, in addition to the mercurinium ion, to describe the electrophilic addition of mercuric salts to olefins. We feel that the reaction described by eq 1, leading to optically active products, may best be described by invoking an intermediate such as **2**. It is difficult to conceive how a four-centered concerted addition or a multicentered intermediate could be compatible with this type of equilibrium. Our results do not allow us to draw any firm conclusions as to the exact nature of the bonding in **2**. However, the essential feature of **2** is the proposed cyclic intermediate which has the structural requirements for a stereospecific reaction.

Whether attack by alcohol on **2** proceeds by front-side displacement or by inversion of configuration, the leav-

ing group in both cases is HgX. In the past, *cis* addition has been observed for strained olefins.²⁸ Although **1** is slightly strained and *cis* approach of the attacking solvent appears to be more accessible, *trans* addition has been the more prevalent direction of attack with olefins⁵ and allenes.^{3,4} The answer to this question and the determination of the absolute configuration of **5** is in progress.

Experimental Section

Optical rotations were measured with a Zeiss photoelectric precision polarimeter and a Rudolph Model 80 polarimeter. Vpc analyses employed a Wilkins Aerograph Model A-90-p. Infrared spectra were recorded on a Perkin-Elmer Model 257 grating spectrophotometer. Melting points were determined with the Hoover-Thomas capillary melting point apparatus and are uncorrected.

General Procedure for the Ethoxymercuration of 1,2-Cyclononadiene. Optically active 1,2-cyclononadiene was prepared by the methylithium induced α elimination of optically active 9,9-dibromo-*trans*-bicyclo[6.1.0]nonane. The 1,2-cyclononadiene employed in all of the experiments described below had $[\alpha]^{25}_D - 81.8^\circ$ (*c* 2.28, methylene chloride) and the optical purity could be as high as 48%. The highest observed rotation for **1** prepared by this method was $[\alpha]^{25}_D - 169^\circ$ (*c* 0.775, methylene chloride).²⁹

All reactions were carried out in absolute ethanol at room temperature for the specified number of hours. In general, the optically active products were collected by vpc, by one injection, utilizing a 3-mm glass tube immersed in a Dry Ice-Acetone bath. The receiver was weighed before and after collection to determine the net weight of the product. After each collection the sample was transferred quantitatively to a volumetric flask and then its rotation was measured. The product was identified by its infrared spectrum in solution or it was recollected and the spectrum was taken neat. The infrared spectrum of each sample of **5** was compared to the spectrum of 3-ethoxycyclononene obtained by the reduction of **4a** that had a *cis* configuration of the double bond. No difficulty was experienced in isolating the optically active 3-ethoxycyclononene by this method without racemization. However, in order to prevent extensive racemization of 1,2-cyclononadiene the injection port temperature was lowered to 90° ; a 3 ft \times 0.25 in. 20% SE-30 column was utilized at $55-65^\circ$, and the temperature of the detector and collector was lowered to approximately 100° . In order to achieve retention times of less than 20 min the flow of He was increased to 150-200 cc/min. Under these conditions **1** racemized less than 1% during isolation.

Ethylmercuric Acetate. a. To a stirring solution of 0.28 g (0.96 mmol) of ethylmercuric acetate in 2 ml of ethanol was added 0.12 g (0.98 mmol) of 1,2-cyclononadiene and 25 μ l of boron trifluoride etherate. After 12 hr the reaction was quenched with 0.10 g of sodium carbonate and 15 ml of water. The aqueous layer was extracted with three 10-ml portions of methylene chloride. The organic phase was dried over anhydrous magnesium sulfate and the solvent was removed at an aspirator. The product, 3-ethoxycyclononene,² was isolated by vpc (6 ft \times 0.25 in. EGS) and 0.1376 g (85.4%) had $[\alpha]^{25}_D + 15.3^\circ$ (*c* 6.88, methylene chloride). The compound was recollected and shown to be optically stable to the isolation procedure and homogeneous to vpc.

b. In a similar experiment 0.20 g (0.69 mmol) of ethylmercuric acetate in 2 ml of ethanol was allowed to react with 0.11 g (0.90 mmol) of 1,2-cyclononadiene and 20 μ l of boron trifluoride etherate for 2.0 hr. The unreacted **1** was quickly distilled into a cold trap and isolation by vpc gave 0.0550 g (50%) that had $[\alpha]^{25}_D - 81.5^\circ$ (*c* 5.50, methylene chloride) for 100% retention of the optical activity of the allene.

Phenylmercuric Acetate. To a stirred solution of 0.277 g (0.82 mmol) of phenylmercuric acetate in 4 ml of ethanol was added 0.106 g (0.86 mmol) of 1,2-cyclononadiene and 25 μ l of boron trifluoride etherate. The reaction mixture was allowed to stir 14 hr and ethanol was removed at an aspirator. The residue was processed as described above by extraction with methylene chloride.

(25) The validity of this suggestion, based on theoretical considerations, obviously requires the resonance stabilization of the allyl cation to be comparable to the radical. Molecular orbital and valence bond calculations give a value of 17-18 kcal/mol for the allyl cation resonance energy.^{26a} More refined calculations suggest that on going from Hückel orbitals to SCF orbitals the decrease in energy is negligible. However, a complete configuration interaction calculation lowers the energy of the allyl cation by 0.32 eV.^{26b} For a general discussion on the allyl system see: L. Salem, "The Molecular Orbital Theory of Conjugated Systems," W. A. Benjamin, Inc., New York, N. Y., 1966, p 68.

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The solvent was removed and the product was isolated by short-path distillation into a cold trap followed by collection by vpc (3 ft \times 0.25 in., SE-30, 140°) which afforded 0.0577 g (42%) of 3-ethoxycyclononene that had $[\alpha]^{25D} + 13.6^\circ$ (*c* 2.885, methylene chloride).

In similar experiments catalyzed by perchloric acid and fluoroboric acid, vpc indicated essentially quantitative conversion of **1** to the allyl ether **5**.

Mercuric Acetate. a. To a solution of 0.319 g (1 mmol) of mercuric acetate in 2.0 ml of ethanol was added 0.122 g (1 mmol) of 1,2-cyclononadiene. The solution was stirred 14 hr, the ethanol was removed at an aspirator, and the residue was dissolved in pentane and filtered. Removal of the solvent gave 0.359 g (84%) of 2-acetoxymercuri-3-ethoxycyclononene (**4a**) as a crude, clear oil. The product was evacuated overnight at reduced pressure (1 mm) and had $[\alpha]^{25D} - 13.7^\circ$ (*c* 32.54, pentane); ir (neat) 1730 (weak), 1580 (broad), 1080, and 790 cm^{-1} . Exclusive formation of the *cis* isomer has also been established by nmr.³⁰

The organomercury compound **4a** (0.3 g, 0.7 mmol) was added to 20 ml of liquid ammonia and 10 ml of ether. A white precipitate was formed that turned brown on addition of 0.065 g (2.8 mmol) of sodium metal. The mixture was stirred for 30 min, and the excess reductant was destroyed by the addition of solid ammonium chloride. Ammonia was allowed to evaporate, and the residue was processed by extraction with methylene chloride. Collection by vpc gave, as a major product, 0.0672 g (57%) of 3-ethoxycyclononene (**5**) that had $[\alpha]^{25D} + 12.4^\circ$ (*c* 6.72, methylene chloride). The material was recollected and 0.0599 g of **5** had $[\alpha]^{25_{365}} + 46.7^\circ$, $[\alpha]^{25_{405}} + 33.9^\circ$, $[\alpha]^{25_{436}} + 27.4^\circ$, $[\alpha]^{25_{546}} + 14.9^\circ$, $[\alpha]^{25_{578}} + 12.9^\circ$, $[\alpha]^{25D} + 12.3^\circ$ (*c* 5.99, methylene chloride).

A minor product (0.0096 g) with a shorter retention time was shown to be the product of reductive cleavage of the allyl ether **5**. Identification as *cis*-cyclononene, contaminated with a trace (<0.25%) of *trans*-cyclononene was made by vpc (8 ft \times 1/8 in. 5% AgNO₃ on TEG) and by comparison of its infrared spectrum with that of an authentic sample. The reduction of the vinylmercury compound should be stereospecific³¹ and since *trans*-cyclononene does not readily isomerize under the reaction conditions³² we feel that oxymercuration under these conditions was stereoselective and afforded greater than 99% *cis* addition. This argument is buttressed by an infrared absorption at 790 cm^{-1} assigned to the *cis* double bond in **5**, and the absence of strong absorption in the vicinity of the 960–980 cm^{-1} characteristic of a *trans* double bond.³³

b. To a stirred solution of 0.0182 g (0.057 mmol) of mercuric acetate in 2 ml of ethanol was added 0.0568 g (0.465 mmol) of 1,2-cyclononadiene and 20 μl of boron trifluoride etherate. The reaction was allowed to stir for 5 hr and 0.0519 g (66.6%) of 3-ethoxycyclononene was isolated by vpc as previously described. The allyl ether **5** had $[\alpha]^{25D} + 12.6^\circ$ (*c* 2.595, methylene chloride) demonstrating that the acidolysis reaction due to the addition of BF₃ does not result in racemization of the product. An infrared spectrum of this material was identical with that of **5** obtained from the reduction of **4a** and **4b**.

c. In a separate experiment 0.196 g of optically active **4a**, $[\alpha]^{25D} - 13.7^\circ$, in 10 ml of chloroform was converted to 2-chloromercuri-3-ethoxycyclononene (**4b**)² by treatment with 20 ml of saturated aqueous sodium chloride solution. The product (0.156 g) was recrystallized from petroleum ether and 0.05 g had mp 113.5–114°. The compound did not exhibit a measurable rotation in methylene chloride solution. However, when **4b** (0.0425 g) was converted back to the acetoxymercuri compound **4a** with silver acetate (0.12 g) in 5 ml of ethanol the isolated crude, oily product had $[\alpha]^{25D} - 12.9^\circ$ (*c* 3.61, pentane) which demonstrates the optical stability, within experimental error, of **4b** prepared by this method.

Mercuric Perchlorate. To a stirred solution of 0.076 g (0.135 mmol) of mercuric perchlorate nonahydrate in 2 ml of ethanol was added 0.111 g (0.91 mmol) of 1,2-cyclononadiene and 25 μl of boron trifluoride etherate. After 10 hr the reaction was quenched and 0.1257 g (82.4%) of 3-ethoxycyclononene was isolated by vpc as previously described; $[\alpha]^{25D} + 12.1^\circ$ (*c* 5.42, methylene chloride).

Mercuric Oxide. To a stirred solution of 0.052 g (0.425 mmol)

of 1,2-cyclononadiene in 1 ml of ethanol was added 0.015 g (0.069 mmol) of red mercuric oxide and 15 μl of boron trifluoride etherate. The clear solution was allowed to stir overnight. The product was isolated as previously described and 0.0519 g (73%) of 3-ethoxycyclononene had $[\alpha]^{25D} + 11.2^\circ$ (*c* 5.19, methylene chloride). In similar experiments the reaction was shown to be at least 90% completed within 1 hr.

Mercuric Sulfate. To a stirred solution of 0.050 g (0.41 mmol) of 1,2-cyclononadiene in 1 ml of ethanol was added 0.040 g (0.135 mmol) of mercuric sulfate and 15 μl of boron trifluoride etherate. The mixture was stirred overnight, and the product was isolated as previously described. Collection by vpc gave 0.0498 g (72%) of 3-ethoxycyclononene that had $[\alpha]^{25D} + 10.5^\circ$ (*c* 4.38, methylene chloride).

The experiment was repeated on 0.053 g of **1**, 0.02 g of mercuric sulfate, and 15 μl of boron trifluoride etherate. The isolation procedure afforded 0.0538 g (74%) of **5** that had $[\alpha]^{25D} + 10.2^\circ$ (*c* 4.62, methylene chloride). The yield and the relative stereospecificity of the reaction was not affected by the amount of mercuric salt utilized.

Mercuric Nitrate. a. To a stirred solution of 0.169 g (0.52 mmol) of mercuric nitrate in 2 ml of ethanol was added 0.054 g (0.44 mmol) of 1,2-cyclononadiene and 20 μl of boron trifluoride etherate. The reaction was stirred 5 hr, and the product was isolated as previously described. Collection by vpc gave 0.0516 g (70.2%) of 3-ethoxycyclononene that had $[\alpha]^{25D} + 9.9^\circ$ (*c* 2.583, methylene chloride).

b. In the absence of boron trifluoride etherate, mercuric nitrate, 0.0209 g (0.064 mmol), and 0.059 g (0.48 mmol) of 1,2-cyclononadiene, were allowed to react for 5 hr as described above. Collection by vpc afforded 0.040 g (50.8%) of 3-ethoxycyclononene that had $[\alpha]^{25D} + 9.9^\circ$ (*c* 2.045, methylene chloride). This experiment again demonstrated that BF₃ had no effect on the stereospecificity of this reaction.

Mercuric Acetate and Mercuric Chloride. A mixture of 0.160 g (0.50 mmol) of mercuric acetate and 0.136 g (0.50 mmol) of mercuric chloride was stirred for 30 min in 10 ml of ethanol. After the addition of 0.128 g (1.05 mmol) of 1,2-cyclononadiene the reaction mixture was allowed to stir overnight. The ethanol was removed and the white solid was recrystallized once from petroleum ether (bp 30–60°) and 0.32 g of **4b** was obtained, mp 107–109°. The chloromercuri derivative was reduced with sodium ammonia as described above and the resulting 3-ethoxycyclononene (**5**) had $[\alpha]^{25D} + 6.1^\circ$ (*c* 8.0, methylene chloride).

Mercuric Fluoride. To a stirred suspension of 0.215 g (0.90 mmol) of mercuric fluoride in 4 ml of ethanol was added 0.127 g (1.03 mmol) of 1,2-cyclononadiene. No reaction was visibly apparent until 25 μl of boron trifluoride etherate was added at which time the mercuric salt quickly dissolved. The reaction mixture stirred overnight, and on removal of solvent a pentane soluble oil was obtained. The oil was taken up in 20 ml of chloroform and stirred for 3 hr with a saturated solution of sodium chloride. After one recrystallization from petroleum ether the white crystalline product (0.2 g) **4b** had mp 114–115° and an infrared spectrum identical with the same compound prepared from mercuric acetate. The organomercuri compound was reduced with sodium-ammonia as described above. Collection by vpc gave 0.0655 g (43.5%) of **5** that had $[\alpha]^{25D} + 1.4^\circ$ (*c* 3.28, methylene chloride).

Mercuric Chloride. a. To a stirred solution of 0.55 g (2.0 mmol) of mercuric chloride in 5 ml of ethanol was added 0.244 g (2.0 mmol) of 1,2-cyclononadiene. The reaction mixture was stirred 14 hr and the ethanolic solution was placed in a freezer. The product was collected by filtration and washed with pentane, and the solvents were removed at reduced pressure. The first crop of crystals (0.20 g) of **4b** had mp 115.5–116.5° (lit.² mp 117.5–118°). A solution of 0.0318 g in 1 ml of methylene chloride-ethanol did not exhibit a measurable rotation. A second crop (0.030 g) had mp 115.5–116.5° after one recrystallization from ethanol. This material was also shown to be optically inactive in the 578–365-m μ region. An infrared spectrum of this material (KBr and CHCl₃) was identical in every respect with the same compound, **4b**, prepared from mercuric acetate and shown to be the *cis* adduct.

The sodium-ammonia reduction of **4b** to **5** was carried out according to the procedure of Gardner² as described above for the reduction of **4a**. Compound **4b** (0.120 g, 0.495 mmol) was treated with 0.045 g (1.95 g-atoms) of sodium metal. The product was collected by vpc and 0.0601 g (72%) of 3-ethoxycyclononene had $[\alpha]^{25_{365}} + 0.9^\circ$, $[\alpha]^{25D} + 0.15^\circ$ (*c* 6.01, methylene chloride).

b. To a stirred solution of 0.33 g (1.22 mmol) of mercuric

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chloride in 2 ml of ethanol was added 0.15 g (1.22 mmol) of 1,2-cyclononadiene. The reaction mixture was stirred for 1.5 hr and the unreacted **1** was quickly distilled into a cold trap. Collection by vpc afforded 0.0188 g of **1** that had $[\alpha]^{25}_D - 35.6^\circ$ (*c* 1.88, methylene chloride). The nonvolatile residue was reduced with sodium ammonia as described above and 0.0170 g of 3-ethoxycyclononene had $[\alpha]^{25}_D + 0.17^\circ$ (*c* 1.70, methylene chloride). The rotation of **5** was the same, within experimental error, as that observed when the reaction time was 14 hr.

In a similar experiment an excess of mercuric salt was utilized and 0.41 g (1.51 mmol) of mercuric chloride in 2 ml of ethanol was allowed to react with 0.10 g (0.82 mmol) of **1** for 2.0 hr. The unreacted 1,2-cyclononadiene was collected by vpc and 0.0132 g had $[\alpha]^{25}_D - 16.3^\circ$ (*c* 1.32, methylene chloride). In both experiments the diene was extensively racemized but its optical purity was considerably greater than that of the product **4b**.

The Stability of 4b in the Presence of Acids. a. To a stirred solution of 0.10 g of **4b** in 5 ml of ethanol was added 0.5 ml of boron trifluoride etherate. The reaction mixture was stirred overnight. The solvents were removed at an aspirator, and only starting material was recovered. Examination of a pentane extract of the residue, by vpc, showed only a trace of 3-ethoxycyclononene.

b. In a separate experiment a quantity of **4b** was treated with dilute hydrochloric acid in ethanol solution and was shown to be stable. However, when **4b** was treated with concentrated hydrochloric acid in ethanol, acidolysis resulted, and the product of the reaction was **5** contaminated with 3-hydroxycyclononene. Optically active **4b** (1.0 mmol) was allowed to stir for 3 hr in the presence of concentrated HCl (1.2 mmol) in 4 ml of ethanol. The allylic ether **5** recovered on reduction of **4b** had $[\alpha]^{25}_D + 12.3^\circ$ (*c* 3.16, methylene chloride) demonstrating the optical stability of **4b** under the reaction conditions.

The Stability of 4b in the Presence of Mercuric Chloride. To a solution of 0.267 g (0.84 mmol) of mercuric acetate in 2 ml of ethanol was added 0.160 g (1.3 mmol) of 1,2-cyclononadiene. The reaction mixture stirred for 2.75 hr and then the volatile compounds were quickly distilled into a cold trap at reduced pressure. The clear oily residue **4a** was converted to **4b** with excess chloride ion as described above. To the crude white solid, **4b**, was added 0.080 g (0.29 mmol) of mercuric chloride and 6 ml of ethanol. The reaction was allowed to stir for 14 hr. The solvent was removed under reduced pressure (0.1 mm) over a 4-hr period. The crude chloromercuric compound and mercuric chloride were reduced in liquid ammonia with 0.06 g of sodium metal as described above. On collection by vpc 0.0682 g of 3-ethoxycyclononene had $[\alpha]^{25}_D + 12.5^\circ$ (*c* 6.82, methylene chloride). This experiment demonstrated that **4b** was also optically stable in the presence of mercuric

chloride and that the product of the reaction of **1** with mercuric acetate after 2.75 hr had the same rotation as the product isolated after 14 hr. In a separate experiment the melting point of **4b** did not change under these reaction conditions.

The unreacted 1,2-cyclononadiene recovered from the above distillate was collected by vpc and 0.03425 g of **1** had $[\alpha]^{25}_D - 75.6^\circ$ (*c* 3.425, methylene chloride) and had retained 92% of its optical purity.

The Stability of 3-Ethoxycyclononene (5). a. **In the Presence of Sodium-Ammonia.** To a stirred solution of 0.034 g of sodium metal in 20 ml of liquid ammonia was added 0.0519 g of **5**, $[\alpha]^{25}_D + 11.2^\circ$ (*c* 5.19, methylene chloride) dissolved in 10 ml of ether. The mixture was stirred for 30 min before the excess sodium was destroyed by the addition of solid ammonium chloride. The 3-ethoxycyclononene was recovered by the method previously described and collection by vpc gave 0.0308 g of **5** that had $[\alpha]^{25}_D + 11.2^\circ$ (*c* 3.08, methylene chloride).

b. **In the Presence of Mercuric Chloride.** An ethanolic solution of 0.05 g of **5** ($[\alpha]^{25}_D + 9.9^\circ$) was stirred overnight with 0.055 g of mercuric chloride and the recovered 3-ethoxycyclononene (0.0384 g) had not racemized; $[\alpha]^{25}_D + 10.2^\circ$ (*c* 1.919, methylene chloride).

c. **In the Presence of Perchloric Acid and Boron Trifluoride Etherate.** To a stirred solution of 0.0468 g of **5**, $[\alpha]^{25}_D + 13.6^\circ$ (*c* 2.34, methylene chloride) in 2 ml of ethanol was added 25 μ l of 11.7 *M* aqueous perchloric acid and 25 μ l of boron trifluoride etherate. The reaction mixture was stirred for 10 hr. Collection by vpc afforded 0.0339 g of 3-ethoxycyclononene that had $[\alpha]^{25}_D + 13.4^\circ$ (*c* 1.695, methylene chloride). In the above three experiments **5** was shown to be optically stable within experimental error.

The Stability of 1,2-Cyclononadiene (1). a. A 50- μ l quantity of **1** was collected by vpc and 0.0405 g had $[\alpha]^{25}_D 79.8^\circ$ (*c* 4.05, methylene chloride). This material was transferred to a solution of 25 μ l of boron trifluoride etherate in 2 ml of ethanol and allowed to stir for 14 hr. The diene **1** was recollected and 0.0203 g had $[\alpha]^{25}_D - 74.9^\circ$ (*c* 2.03, methylene chloride). The allene had retained greater than 90% of its optical activity.

b. To a solution of 0.105 g of **4b** in 6 ml of ethanol was added 0.05 g of **1**. The reaction was allowed to stir 6.5 hr and the diene was quickly distilled into a cold trap. Collection by vpc gave 0.0301 g of 1,2-cyclononadiene that had $[\alpha]^{25}_D - 81.7^\circ$ (*c* 3.01, methylene chloride). The diene did not exhibit a measureable degree of racemization.

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