leave 10.6 mg of a crude mixture of the hemiacetals, **86** and **87**, $\nu_{max}$ 3554 and 1731 $cm^{-1}$, which was dissolved in 1 ml of dry methylene chloride. To the solution was added 53 mg of Collins' reagent[20] under nitrogen. The suspension was stirred for 25 min, poured into ice–water, and extracted with ether–methylene chloride (4:1). The organic extract was washed with 2 *N* sulfuric acid (1 ml) and water, dried, and evaporated to leave 9.6 mg of a crude mixture of isomeric lactones, **88a** and **89a**. Preparative tlc of the above mixture on silica gel (doubly developed with *n*-hexane–methanol (10:1)) furnished 0.9 mg of *dl*-gibberellin $A_{15}$ methyl ester **88a** and 1.2 mg of the isomeric lactone ester **89a**. Crystallization of the former component from ether–pentane gave 0.6 mg of *dl*-gibberellin $A_{15}$ methyl ester $A_{15}$ **88a**, mp 168–170°. Its ir (in chloroform), mass spectrum, tlc (silica gel G, ethyl acetate–benzene (9:1)), and glc (1% OV-1 and 1% QF-1) data were identical with those of an authentic sample. Crystallization of the latter component from ether–pentane gave 0.6 mg of the isomeric lactone ester **89a**: mp 114–116°; $\nu_{max}$ 1728, 1656, 1162, 1156, and 884 $cm^{-1}$; mass, molecular ion *m/e* 344; nmr $\tau$ 9.20 (3 H, s, $CH_3$).

***dl*-Gibberellin $A_{15}$ 1.** A mixture of 1.7 mg of the *dl*-gibberellin $A_{15}$ methyl ester **88a** and 4 mg of triphenylphosphine, 8 mg of anhydrous lithium iodide, and 0.4 ml of dry γ-collidine was refluxed for 50 min under argon. The reaction mixture was cooled, acidified with 1.6 ml of 3 *N* hydrochloric acid, and extracted with ether–methylene chloride (3:1). The organic layer was extracted successively with 2 *N* sodium hydroxide (0.8 ml) and water. After acidification (to pH 3) of the aqueous sodium hydroxide extract with dilute hydrochloric acid. the aqueous layer was extracted with chloroform–methanol (9:1). The organic extract was washed with water, dried, and evaporated to leave 1.7 mg of a residue, which was crystallized from acetone–pentane to furnish 0.6 mg of *dl*-gibberellin **1**, mp 236–237°. This sample showed an ir spectrum (in chloroform), mass spectrum, and tlc (Woelm silica gel, benzene–ethyl acetate (4:1), isopropyl ether–acetic acid (95:5)) completely identical with those of an authentic sample of **1** (the naturally occurring optically active compound).

**The Lactone Acid 89b.** A mixture of 2.7 mg of the isomeric lactone ester **89a**, triphenylphosphine (4.0 mg), anhydrous lithium iodide (8 mg), and dry γ-collidine (0.4 ml) was treated as above to afford 2.1 mg of an acidic residue, which was crystallized from acetone–pentane to furnish 0.8 mg of the lactone acid **89b**, mp 187–189°. Recrystallization raised the melting point to 197–198°: $\nu_{max}$ 1727, 1713, 1656, 1147, and 885 $cm^{-1}$; mass, molecular ion *m/e* 330.

**Bioassay. Preparation of Test Solutions.** *dl*-Gibberellin $A_{15}$ **1** (60 μg) was dissolved in water (6 ml) at 70° to give a $3 \times 10^{-5}$ *M* solution. The isomeric lactone **89b** (60 μg) was also dissolved in water (6 ml) at 70° to give a $3 \times 10^{-5}$ *M* solution. These solutions were diluted with water to give $3 \times 10^{-6}$ *M* solutions.

**Bioassay Procedures.** The rice seedling growth test procedure as follows. Seeds of rice (*Oryza sativa*, var. Norin No. 29) were soaked in EtOH for 10 min and then in a saturated solution of bleaching powder for 1 hr. The sterilized seeds were transferred into a large petri dish containing sterilized water of 1 cm depth. The petri dish was kept at 30° for 48 hr under white fluorescent and incandescent lamps (about 5000 lx). Germinating seeds having 3–5 mm coleoptiles were employed for further use. These seeds were placed in test tubes (3 × 10 cm), 15 to one test tube, containing 1.35 ml of aqueous test solution. After covering the tubes with a polyethylene sheet, they were kept for 5 days under white fluorescent and incandescent lamps (about 5000 lx). The second leaf sheathes of the seedlings were then measured and compared with those of control plants, grown in water alone.

**Acknowledgments.** We wish to thank the late Mr. M. Sahori, Mr. M. Yamaguchi, and Mr. Y. Haga for their participation in this work. We are very grateful to Professor Y. Isogai, Biological Institute, College of General Education, University of Tokyo, for kindly carrying out the bioassay of the synthetic materials.

# The Stereochemistry of Addition Reactions of Allenes. V. Stereoselective Bromination of 1,2-Cyclononadiene

**Larry R. Byrd[1] and Marjorie C. Caserio*[2,3]**

*Contribution from the Department of Chemistry, University of California, Irvine, California 92664.* *Received January 18, 1971*

**Abstract:** Bromine addition to partially resolved 1,2-cyclononadiene has been found to give a mixture of *optically active* normal and transannular monoadducts. In carbon tetrachloride the major product is *cis*-2,3-dibromocyclononene; the minor product is *cis*-1,4-dibromocyclononene formed by a 1,5-hydride shift. In methanol, the major products are *cis*-1-bromo-4-methoxycyclononene and *cis*-2-bromo-3-methoxycyclononene formed in the ratio of 3:2, respectively. Induction of asymmetry in the normal 2,3 adducts and in the transannular 1,4 adducts is discussed in terms of the involvement of dissymmetric transition states and reaction intermediates. Absolute configuration of each of the derived 1,4 adducts is assigned by reason of the absolute configuration of the starting allene and the nature of the stereoselective reactions by which they are formed. The 2,3 adducts are evidently formed by a mechanism of trans electrophilic addition.

The dissymmetry inherent in 1,3-disubstituted allenes provides a valuable probe of the stereochemistry of addition reactions to the allenic system. By this approach it has been established that mercuric acetate and halogens react with (*R*)-(−)-2,3-pentadiene in methanol to give monoadducts by way of net trans addition of the attacking reagents to one of the double bonds.[3,4] The orientation of addition is such that the attacking electrophile combines exclusively with the central allenic carbon to form a mixture of cis and trans isomeric adducts in which the trans isomer predominates (83–94%). The intermediacy of dissymmetric bridged ions has been suggested to explain the stereoselectivity observed (eq 1).

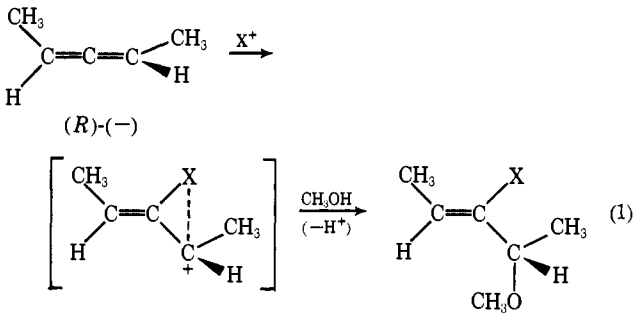
Electrophilic additions to other optically active allenes have been reported. Reaction of (+)-2,2-dimethyl-3,4-hexadien-1-ol with 2,4-dinitrobenzene-

(1) NDEA Fellow, 1967–1970.

(2) The authors gratefully acknowledge the support received from the donors of the Petroleum Research Fund of the American Chemical Society (PRF 2357-A1,4).

(3) Part IV: M. Findlay, W. L. Waters, and M. C. Caserio, *J. Org. Chem.*, **36**, 275 (1971).

(4) W. L. Waters, W. S. Linn, and M. C. Caserio, *J. Amer. Chem. Soc.*, **90**, 6741 (1968); **92**, 4018 (1970).

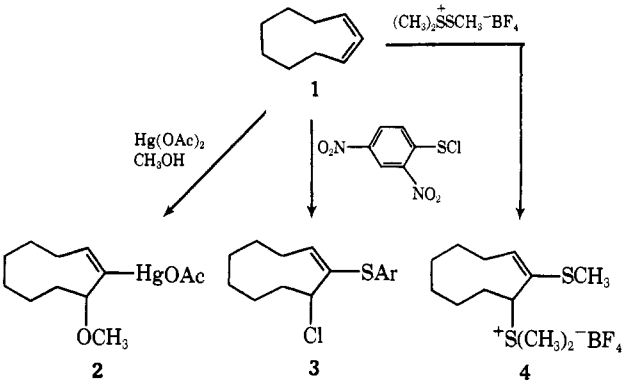


(*R*)-(−)

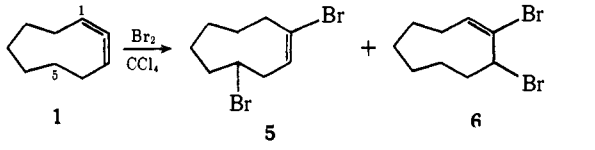
X = HgOAc, Cl, Br, or I

(1)

sulfenyl chloride was observed to give an optically active adduct whereas bromine addition gave a racemic adduct.[5] Oxymercuration and addition of sulfenyl compounds to 1,2-cyclononadiene **1** are reported to give cis monoadducts exclusively. This contrasts with the related reactions of 2,3-pentadiene, which give mainly trans monoadducts. Thus, methoxymercuration of **1** with mercuric acetate in methanol gives only *cis*-2-acetoxymercuri-3-methoxycyclononene[6,7] (**2**). Optically active **1** on oxymercuration has been found to give optically active adducts of varying optical purity depending on the mercury electrophile used.[7] Addition of 2,4-dinitrobenzenesulfenyl chloride[8] and dimethylthiomethylsulfonium fluoroborate[9] gives the cis adducts **3** and **4**, respectively.



Bromine addition to **1** has also been investigated and was first reported to form a 60:40 mixture of *trans*- and *cis*-2,3-dibromocyclononene,[10] respectively. Subsequently, Reese and Shaw[11] reported convincing evidence that the major product is not the trans 2,3 isomer but is *cis*-1,4-dibromocyclononene (**5**) which apparently arises by way of a transannular 1,5-hydride shift.



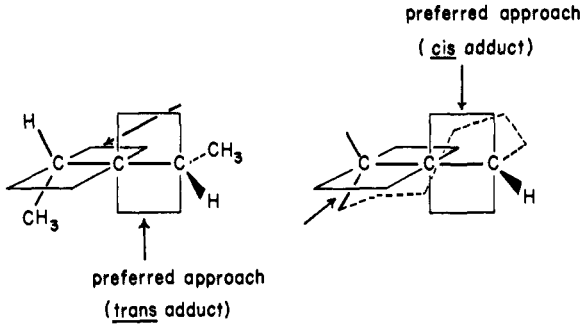
Bromination therefore differs from oxymercuration and sulfenylation of **1** in that transannular addition is not observed in the two latter reactions whereas it represents the major reaction pathway in bromination. This suggests that considerably more carbonium ion character develops at a terminal allenic carbon of **1** in bromination than in oxymercuration and sulfenylation, possibly to the extent of involving open rather than bridged ion intermediates. It was, therefore, of considerable interest to examine the stereochemical course of bromine addition to optically active 1,2-cyclononadiene since the results are expected to reflect the symmetry characteristics of the transition states and carbonium ion intermediates involved. We were particularly interested to determine whether or not optical activity could be induced in the transannular addition product **5** since this information could have important mechanistic implications concerning the hydride transfer process. While we have not yet explored the generality of transannular addition with respect to other halogens, we report here the results of bromine addition to optically active **1** in carbon tetrachloride as an inert solvent and in methanol as a nucleophilic solvent.

## Results

**Resolution of 1,2-Cyclononadiene.** A partial resolution of **1** was achieved by asymmetric hydroboration of excess **1** with (+)-*sym*-tetraisopinocampheyldiborane. The procedure used was basically that reported previously for the partial resolution of 2,3-pentadiene[4] and is described in more detail in the Experimental Section. Starting with (−)-α-pinene of 92% optical purity the unreacted 1,2-cyclononadiene recovered typically had a specific rotation of $[\alpha]_D$ +26°. Based on an estimate of 170–175° for the specific rotation of optically pure **1**,[12a] partially resolved **1** of $[\alpha]_D$ 26° corresponds to about 15% optical purity. Asymmetric synthesis of **1** has been achieved starting with optically active *trans*-cycloöctene of known configuration,[12b] and the absolute configuration of the (−)-enantiomer has been established as *S*[13] and is in accord with Brewster's rules which may be used to predict the configuration from the sign of rotation.[14] Accordingly, we conclude that partial resolution of **1** using (−)-α-pinene affords (*R*)-(+)-**1**.

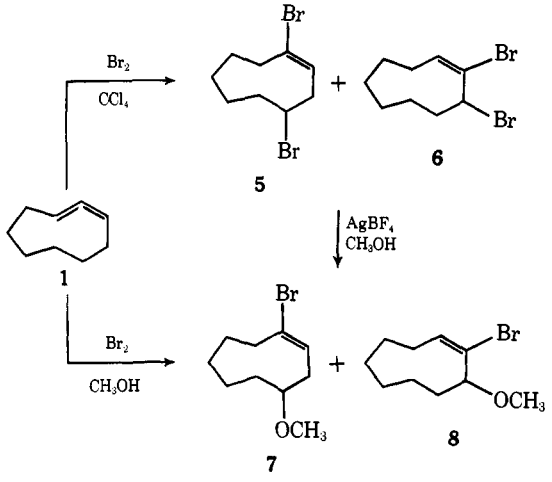
It is interesting to note that partial resolution of 2,3-pentadiene and 1,2-cyclononadiene by the method of asymmetric hydroboration starting with (−)-α-pinene leads to the recovery of allenes enriched in the *R* enantiomer. Stereoselectivity in the hydroboration of the open-chain allene is therefore the same as that observed for the cyclic allene, despite the fact that electrophilic reagents approach 2,3-pentadiene to give trans monoadducts preferentially, whereas these same reagents approach 1,2-cyclononadiene to give only cis monoadducts (see below). The stereoselectivity observed on asymmetric hydroboration of allenes therefore appears to be independent of which side of the allenic system the asymmetric reagent attacks.

(5) T. L. Jacobs, R. Macomber, and D. Zunker, *J. Amer. Chem. Soc.*, **89**, 7001 (1967).
(6) W. L. Waters and M. C. Caserio, unpublished results in this laboratory; see also R. K. Sharma, B. A. Shoulder, and P. D. Gardner, *J. Org. Chem.*, **32**, 241 (1967).
(7) R. D. Bach, *J. Amer. Chem. Soc.*, **91**, 1771 (1969).
(8) T. L. Jacobs and R. Macomber, *J. Org. Chem.*, **33**, 2988 (1968).
(9) D. Ralston and M. C. Caserio, unpublished results, this laboratory.
(10) D. K. Wedegaertner and M. J. Millam, *J. Org. Chem.*, **33**, 3943 (1968).
(11) C. B. Reese and A. Shaw, *J. Amer. Chem. Soc.*, **92**, 2566 (1970).
(12) (a) W. R. Moore, R. D. Bach, and T. M. Ozretich, *ibid.*, **91**, 5918 (1969); (b) A. C. Cope, W. R. Moore, R. D. Bach, and H. J. S. Winkler, *ibid.*, **92**, 1243 (1970).
(13) W. R. Moore, H. W. Anderson, S. D. Clark, and T. M. Ozretich, *ibid.*, **93**, 4932 (1971).
(14) J. H. Brewster, *ibid.*, **81**, 5475 (1959); J. H. Brewster, *Top. Stereochem.*, **2**, 1 (1967).



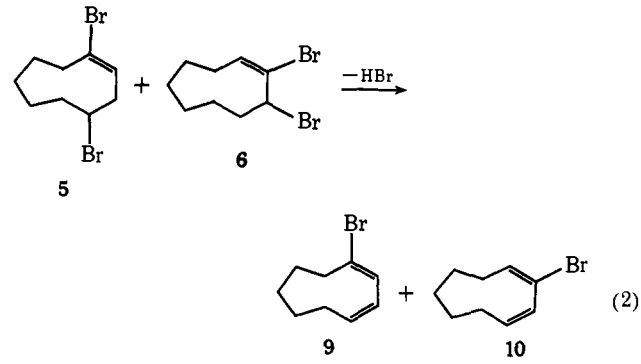

**Bromination in Carbon Tetrachloride.** The reaction of racemic **1** with an equimolar amount of bromine in carbon tetrachloride was investigated over a wide temperature range, −78 to +30°. At 30° an 85% yield of a 39:61 mixture of *cis*-1,4- and *cis*-2,3-dibromocyclononene, **5** and **6**, respectively, was obtained. Structure was assigned by comparison of the nmr spectra of the products with the spectra reported for **5** and **6**.[10,11] The observed product ratio was quite reproducible, but at no time could we achieve the 60:40 mixture of **5** and **6** reported by Wedegaertner and Millam[10] and Reese and Shaw[11] for which we have no adequate explanation. Changes in the product ratio with temperature were noted but the major product was consistently observed to be the cis 2,3 adduct **6**. Structure was confirmed by the quantitative conversion of a 39:61 mixture of **5** and **6** to 35:65 mixture of the corresponding homoallylic and allylic methyl ethers, **7** and **8**, respectively, on treatment with methanolic silver tetrafluoroborate (Scheme I). The products,

**Scheme I**




**7** and **8**, were identical with those obtained directly by bromination of **1** in methanol and independently characterized as described subsequently in the paper.

Analysis of the dibromides by glpc resulted in extensive decomposition under most of the column conditions employed. The decomposition products were isolated by preparative glpc and identified as *cis,cis*-1-bromo-1,3-cyclononadiene (**9**) and *cis,cis*-2-bromo-1,3-cyclononadiene (**10**) by reason of the identity of their nmr spectra with those reported in the literature[15,16] (eq 2).

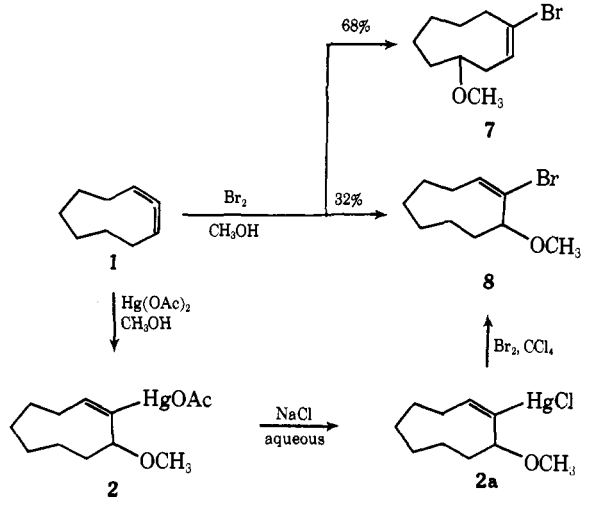



(2)

Bromination of (*R*)-(+)-**1**, $[\alpha]^{28}D$ +26.5 ± 0.1° (neat), in carbon tetrachloride gave a 39:61 mixture of **5** and **6** which, after distillation, had $[\alpha]^{28}D$ +2.38 ± 0.05° (*c* 56, $CDCl_3$). Solvolysis of the 39:61 mixture of optically active **5** and **6** in methanolic silver tetrafluoroborate produced a 35:65 mixture of **7** and **8** which collectively had $[\alpha]^{28}D$ +1.00 ± 0.05° (*c* 91, $CHCl_3$).

**Bromination in Methanol.** Addition of methanolic bromine to an equimolar amount of racemic **1** in methanol produced two major products (78%), **7** and **8**, in the ratio of 68:32. Their nmr spectra were identical with the products of methanolysis of **5** and **6** (Scheme I) and the spectrum of **8** was identical with that reported by Baird and Reese[15] for 2-bromo-3-methoxycyclononene. The cis 2,3 adduct **8** was unequivocally characterized by the reaction sequence of Scheme II.

**Scheme II**




Thus the product of methoxymercuration of **1** was converted by way of the corresponding chloromercuri derivative **2a** to 2-bromo-3-methoxycyclononene by treatment with bromine in carbon tetrachloride. The product was identical in all respects with **8** obtained from **1** on direct bromination in methanol. It is noteworthy that the major product of bromination in methanol is the transannular adduct **7**, whereas, in carbon tetrachloride, we observed the major product to be the normal adduct **6**.

Two minor products of bromination of **1** in methanol, comprising about 20% of the product mixture, were found to be identical in all respects (nmr, glpc) with the dehydrobromination products of **5** and **6**, namely, *cis,cis*-1-bromo- and *cis,cis*-2-bromo-1,3-cyclononadiene, **9** and **10**, respectively. Two other minor

(15) M. S. Baird and C. B. Reese, *J. Chem. Soc. C*, 1803 (1969).
(16) We are indebted to Professor C. B. Reese for giving us the spectral data for 10 prior to publication.

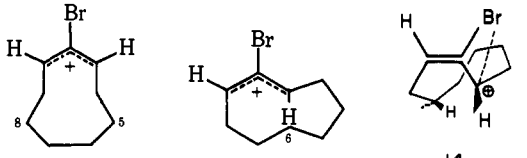
products (about 5% of the total reaction mixture) of long retention time were isolated with difficulty by preparative glpc and found to be spectrally identical with the dibromides **5** and **6**.

Bromination of (*R*)-(+)-**1**, $[\alpha]^{28}D$ +23.40 ± 0.05° (neat), in methanol produced a 68:32 mixture of **7** and **8** which after distillation showed $[\alpha]^{28}D$ +7.96 ± 0.05° (neat). The isomeric bromo ethers were isolated by preparative glpc and their optical rotations measured separately. The sample of **8**, contaminated with 9% of **7**, showed $[\alpha]^{28}D$ +6.2 ± 0.2° (*c* 12, $CHCl_3$), while pure **7** exhibited $[\alpha]^{28}D$ +6.26 ± 0.05° (*c* 10, $CHCl_3$). A high boiling fraction consisting of 70% dibromides **5** and **6** and 30% **7** and **8** showed $[\alpha]^{28}D$ +12.92 ± 0.05° (*c* 40, $CHCl_3$). Reduction of **8** having $[\alpha]D$ +6.80 ± 0.2° (*c* 9, $CHCl_3$) with sodium in ammonia gave (−)-3-methoxycyclononene (**11**) $[\alpha]D$ −2.81 ± 0.05° (*c* 16, $CHCl_3$) for which the *R* configuration has been established.[17]

## Discussion

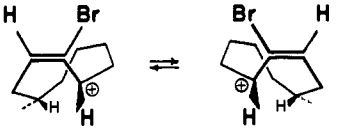
The most interesting result of the bromination studies of (*R*)-(+)-1,2-cyclononadiene is the observed induction of optical activity in both the normal 2,3 adducts **6** and **8** and the transannular adducts **5** and **7**. Stereospecificity in reactions involving transannular hydride shifts is not without precedent and has been demonstrated principally in the solvolysis of cycloalkenyl oxides. For example, hydration of *cis*-cycloöctene oxide leads to a fair yield of *cis*-1,4-cycloöctanediol (no trans) while that of *trans*-cycloöctene oxide gives *trans*-1,4-cycloöctanediol (no cis).[18] This result has been interpreted in terms of either a completely concerted solvolysis or of carbonium ion intermediates that retain substantial tetrahedral character.[18] In contrast, however, hydration of both *cis*- and *trans*-cyclononene oxides leads to a mixture of cis and trans 1,5-diols by a nonstereospecific 1,4-hydride transfer.[19] There is, therefore, little resemblance between the nonselective 1,4-transannular shifts of cyclononene oxides and the stereoselective 1,5-transannular shifts observed in the bromination of 1,2-cyclononadiene. The conformations of the transition states involved in the transannular reactions of the two nine-membered ring systems must therefore be very different. As will shortly be described, the transannular reactions of 1,2-cyclononadiene more closely resemble those of *trans*-cycloöctene and related compounds.

The induction of optical activity in the products of bromination of **1** unequivocally precludes the exclusive intervention of a symmetrical resonance-stabilized allylic ion of the type implied in structure **12**. Acknowledging that nucleophilic attack from one side of the allylic plane of **12** might be favored over the other due to puckering of the methylene chain, racemic products would still result since attack at either terminus is equally probable on a given side. Furthermore, molecular models clearly indicate that **12** is a very unlikely precursor to the transannular products since the migrant hydrogens at C-5 and C-8 are not proximate to the carbonium ion centers. Formation of a "planar" ion such as **13** also seems unlikely since models indicate that a 1,6 hydride shift should be greatly favored over the observed 1,5 hydride shift, contrary to the experimental results. The absence of products of the trans configuration is also an argument against the participation of **13**.




12 13 14

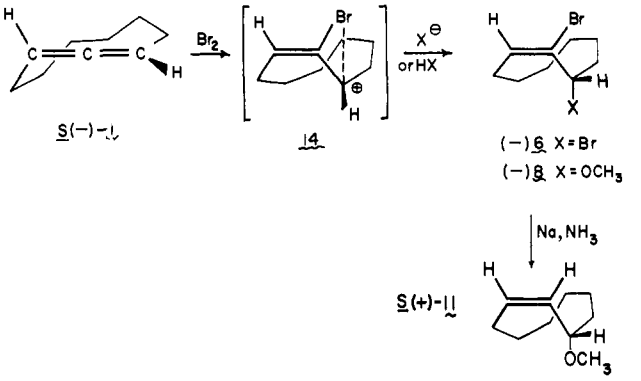
A plausible intermediate responsible for the normal and transannular addition products is the bridged structure **14**. This intermediate corresponds to an orientation in which the electrophile approaches the least hindered side of the allenic system (*i.e.*, from outside the ring) to attack the central allenic carbon. Nucleophilic attack of $Br^-$ or $CH_3OH$ at the terminal allenic carbon could lead to optically active 2,3 adducts, **6** or **8**, while internal transfer of $H:^-$ to this site accompanied by nucleophilic attack at the developing homoallylic carbonium ion center could lead to optically active 1,4 adducts **5** or **7**. The observed stereoselectivity may equally well be accommodated by a dissymmetric *open* allylic carbonium ion **14a** which reacts to give products *faster* than it interconverts with its enantiomer **14b**. Since an "immobile" dissymmetric open ion is virtually indistinguishable from the bridged species **14**, we have chosen for purposes of further discussion to formulate the reaction in terms of the bridged ion **14**.




14a ⇌ 14b

The important point to note is that bromination of (*R*)-(+)-**1** in methanol gives (+)-**8** which must have the *R* configuration since on reduction it gives (*R*)-(−)-**11**[17] (see Scheme III, drawn here for (*S*)-(−)-**1**).

**Scheme III**




This means that *bromination of 1,2-cyclononadiene in methanol is a stereoselective trans (anti) addition.* By analogy, we assume that bromination in carbon tetra-

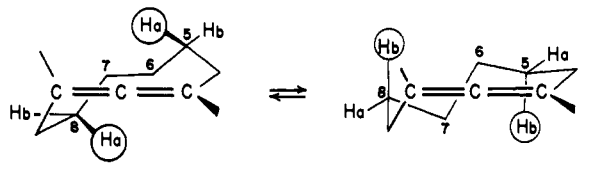
(17) We are indebted to Professor Robert D. Bach, Wayne State University, for providing us with the details of his work establishing the absolute configuration of 3-methoxycyclononene in advance of publication.

(18) A. C. Cope, M. M. Martin, and M. A. McKervey, *Quart. Rev., Chem. Soc.*, 20, 119 (1966), and references cited therein.

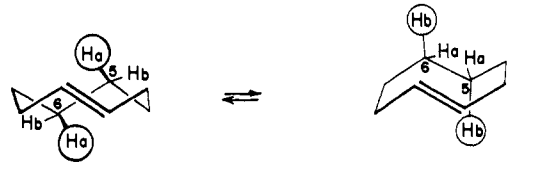
(19) V. Prelog, K. Schenker, and W. Küng, *Helv. Chim. Acta*, **36**, 471 (1953).

chloride also proceeds by a trans (anti) mechanism and that (+)-2,3-dibromocyclononene has the *R* configuration. These results parallel those obtained on bromination of 2,3-pentadiene which also proceeds by a stereoselective mechanism of trans addition.[3,4]

Formation of optically active 1,4 adducts **5** and **7** requires that a methylene hydrogen at C-5 (or C-8) of **1** be transferred stereoselectively as hydride to the developing carbonium ion center at C-1 (or C-3) in a 1,5 shift. Nucleophilic attack at C-5 (or C-8) to give the product may either be synchronous with or subsequent to the hydride transfer step. In either event, the nucleophile must attack stereoselectively in order for one enantiomer to be formed preferentially. The question of major interest is which of the two methylene hydrogens at C-5 (or C-8) is transferred. Models suggest that the starting enantiomer of **1** may exist in diastereomeric conformations **1a** and **1b**, that are interconverted by rotation of the C(6)–C(7)methylene unit through the loop of the ring. In this respect, 1,2-cyclononadiene resembles *trans*-cycloöctene **15** which also has two elements of dissymmetry—one arising from the rigidity imposed by the double bond and the other from a barrier to rotation of the C(5)–C(6) methylenes through the ring.[20,21] The barrier to rotation involving the single bond is not known quantitatively but it is apparently comparable to that involving the analogous rotation of the double bond through the ring.[20] The major point we wish to make in drawing analogy between 1,2-cyclononadiene and *trans*-cycloöctene is the relationship between the diastereomeric conformations of **1** and **15**. Conformations of **1a** and **15a** both show the proximity of the C-5 methylene hydrogen (labeled as Ha) to C-1, and this hydrogen is therefore implicated in 1,5-transannular hydride shifts which are common to both compounds. Transfer of

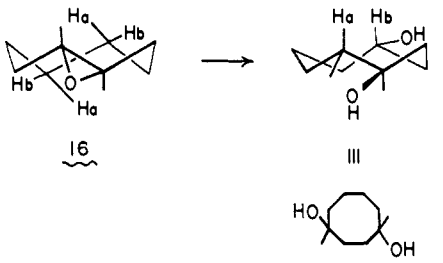


1a 1b



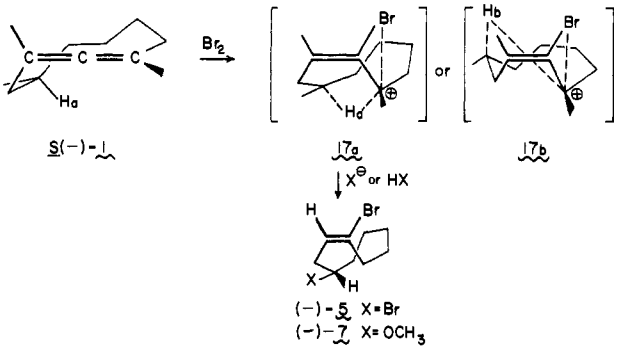
15a 15b

the other methylene hydrogen (labeled as Hb) would have to occur by way of the conformations **1b** and **15b**. However, according to models, this hydrogen does not approach the migration terminus as closely or as comfortably as Ha in **1a** and **15a**, so migration of Hb appears less facile than that of Ha. Evidence for this may be found in the cycloöctene series. Hydration of *trans*-cycloöctene oxide (**16**) gives *trans*-1,4-cycloöctanediol free of the cis isomer.[18] This means that Ha in **16** is transferred in a 1,5 hydride shift since migration of Hb would lead to the cis diol.



16 III

The same conclusions as to which of the C-5 hydrogens of (*R*)-(+)-**1** may be expected to migrate may be reached from a consideration of the two possible diastereomeric transition states **17a** and **17b**. Thus, in **17a**, Ha is disposed very favorably toward transfer to the carbonium ion center in a near-planar six-membered transition state free of any apparent strain. In **17b**, however, migration of Hb appears to involve considerable torsional strain in the transition state with severe interference from the C-9 methylene hydrogens. We conclude therefore that **17a** is the preferred transition state for hydride transfer. Based on the further assumption that the product-forming step involves attack of the entering nucleophile to the rear of the departing hydride, we assign the *S* configuration to (−)-**5** and (−)-**7**.



S(−)-1 17a 17b

(−)-5 X=Br
(−)-7 X=OCH$_3$

The degree of stereospecificity of addition to **1** cannot be inferred from the present data since the optical purity of the products is not known. It is worth noting, however, that bromination of **1** in methanol leads to dibromides **5** and **6** of considerably higher optical purity than bromination of **1** in carbon tetrachloride. The origin of this solvent effect is not known with certainty but it seems likely to be indirectly related to the HBr formed by the *in situ* dehydrobromination of **5** and **6**; the acid so formed may partially racemize the reactant or the product.

A final point of some interest is the observation that a mixture of optically active dibromides **5** and **6** solvolyzes in methanolic silver nitrate to an *optically active* mixture of bromo ethers **7** and **8** with only slight scrambling of the 2,3:1,4 isomer ratio. We have also observed that methanolysis of pure *cis*-2-tosyl-3-iodocyclononene proceeds to give a 72:18 mixture of *cis*-2-tosyl-3-methoxycyclononene and *cis*-1-tosyl-4-methoxycyclononene, respectively. Thus, solvolysis of allylic halocyclononenes proceeds in part by way of transannular 1,5 hydride transfer.

(20) G. Binsch and J. D. Roberts, *J. Amer. Chem. Soc.*, 87, 5157 (1965).
(21) P. C. Manor, D. P. Shoemaker, and A. S. Parkes, *ibid.*, 92, 5260 (1970).

## Experimental Section

All nmr spectra were recorded with a Varian A-56/60 spectrometer; chemical shifts are reported in parts per million downfield from internal TMS. Optical rotation measurements were taken with a Zeiss polarimeter, Model No. 53194, reading to 0.01°. Gas chromatographic analyses and collections employed a Varian series 200 thermal conductivity gas chromatograph equipped with a 20 ft × 3/8 in. aluminum column packed with 20% SE-30 on Chromosorb W (AW, DMCS, 45–60) and a 10 ft × 3/8 in. Pyrex column packed with 10% Carbowax 20M on Chromosorb G (AW, DMCS, 60–80) as noted below. All melting points were taken with a Büchi heated oil bath in unsealed capillaries and are uncorrected.

**(±)-1,2-Cyclononadiene** was prepared in 87% yield from the reaction of *cis*-9,9-dibromobicyclo[6.1.0]nonane with ethereal methyllithium according to the procedure detailed by Skattebøl and Solomon.[22]

**Partial resolution of (±)-1,2-cyclononadiene** was accomplished essentially by the method described earlier for 2,3-pentadiene.[4] Better yields of recovered allene, higher optical purities, and easier work-up were achieved, however, by a few modifications in procedure.[23] In a typical resolution using this modified procedure, boron trifluoride etherate (17.5 g, 0.123 mol) was added to a stirred solution of (−)-α-pinene[24] (33.5 g, 0.246 mol) and sodium borohydride (5.1 g, 0.135 mol) in 70 ml of dry triglyme at 0°. The mixture was stirred and maintained at 0° for about 20 hr in order to achieve the maximum consumption of α-pinene. At this stage, the suspension of *sym*-(+)-tetraisopinocampheyldiborane in triglyme was cooled to −12° and to it was added (±)-1,2-cyclononadiene (30 g, 0.246 mol) all at once. After stirring the mixture for a further 2.5 hr at −12°, unreacted 1,2-cyclononadiene was recovered by flash distillation (50–70° (4 mm)) followed by extraction with water to remove triglyme from the distillate. Fractional distillation afforded 12.1 g (80%) of 1,2-cyclononadiene having $[\alpha]^{28}D$ +26.53 ± 0.05° (neat), bp 63–65° (15 mm).

**Addition of bromine to (±)-1,2-cyclononadiene in carbon tetrachloride** was carried out exactly as reported by Wedegaertner and Millam,[10] except that the quantity of allene was scaled to 4.5 g (0.037 mol). The residual yellow oil was vacuum distilled to afford 1.6 g of a forerun (75–88° (0.3 mm)) and 8.8 g (85%) of slightly yellow oil (90–91° (0.3 mm)). Analysis of the forerun by glpc [150°, 10 ft × 3/8 in. Pyrex, 5% Carbowax 20 M on Chromosorb G (AW, DMCS, 60–80)] showed two products of similar retention time in about a 1:1 ratio. They were collected preparatively [150°, 20 ft × 3/8 in. aluminum, 20% SE-30 on Chromosorb W (AW, DMCS, 45–60)] and characterized as *cis,cis*-1-bromo- and *cis,cis*-2-bromo-1,3-cyclononadiene on the basis of their nmr spectra which are virtually identical with those reported for authentic **9**[16] and **10**.[15] The higher boiling major fraction was characterized by nmr as a 39:61 mixture of *cis*-1,4- and *cis*-2,3-dibromocyclononene, respectively (integration of methine protons). The spectrum of the isomeric dibromides was entirely consistent with the spectra reported by Wedegaertner and Millam[10] and Reese and Shaw[11] for compounds **5** and **6**. Thus, the normal adduct as a 50% solution in $CDCl_3$ had δ 6.12 (t, $J$ = 8.8 Hz, 1, vinyl), 5.18 (dd, $J$ = 5 and 12 Hz, 1, allylic methine), and the transannular adduct had δ 5.86 (t, $J$ = 8.8 Hz, 1, vinyl), 4.18 (m, 1, methine). The dibromides could not be well resolved under most glpc column conditions; only **9** and **10** were detected after injection of the mixture. Decomposition was minimized and nearly complete resolution of **5** and **6** was achieved using the 10 ft × 3/8 in. Pyrex column packed as above with a reduced injection port temperature (195°) and increased flow rate (175 cm³/min). The reaction was repeated at −78° (Dry Ice–acetone) and −15° (ice–salt) with similar results. Small changes in the relative distribution of **5** and **6** were observed with changing temperature, but the major product was consistently observed to be the normal adduct **6**.

**Silver-Assisted Methanolysis of (±)-*cis*-2,3- and 1,4-Dibromocyclononene.** In 40 ml of anhydrous methanol was dissolved 2.00 g (0.0071 mol) of a 61:39 mixture of (±)-*cis*-2,3- and *cis*-1,4-dibromocyclononene. Methanolic silver tetrafluoroborate was added dropwise to the magnetically stirred solution over 5 min until the supernatant failed to precipitate AgBr. After stirring for 15 min, the solution was taken up in 75 ml of ether and washed with three successive 50-ml portions of 10% aqueous $NaHCO_3$ and thereafter with distilled water (three times). The ethereal solution was dried over $MgSO_4$ and filtered, and the ether was evaporated. The residual slightly yellow oil (1.3 g, 79%) was shown by nmr to be a 65:35 mixture of (±)-*cis*-2-bromo-3-methoxy- and *cis*-1-bromo-4-methoxycyclononene (integration of O–$CH_3$ signals). Product assignment was based on the identity of the major product (nmr, glpc) to *cis*-2-bromo-3-methoxycyclononene formed *via* methoxymercuration of (±)-**1** (Scheme II; see details below). Also, the spectrum of the mixture was identical with that of the products of bromination of (±)-**1** in methanol. Finally, the nmr spectrum of the major product was identical with that of authentic *cis*-2-bromo-3-methoxycyclononene.[16] A 20% solution of the minor product in $CDCl_3$, *cis*-1-bromo-4-methoxycyclononene, showed the following nmr spectrum: δ 5.88 (t, 1, vinyl), 3.22 (s, 1, *O*-methyl), 3.2 (m, 1, methine), 2.1–2.9 (m, 4, allylic), 1.5 (m, 8, methylene). Separation of isomers *via* glpc was easily achieved using either column described above at 150°.

**Addition of bromine to (*R*)-(+)-1,2-cyclononadiene in carbon tetrachloride** was carried out exactly as described for the racemic material, except that **1** having $[\alpha]^{28}D$ +26.53 ± 0.05° (neat) was used. The crude undistilled oil containing a few per cent of (*R*)-(+)-**1** showed $[\alpha]^{28}D$ +2.59 ± 0.05° (neat). After fractional distillation as above, the pure 39:61 mixture of (+)-**5** and **6** showed $[\alpha]^{28}D$ +2.38 ± 0.05° (*c* 56, $CDCl_3$).

**Silver-assisted methanolysis of (+)-*cis*-2,3- and 1,4-dibromocyclononene** was carried out exactly as for the racemic material except that a 61:39 mixture of **5** and **6** of $[\alpha]^{28}D$ +2.38 ± 0.05° (*c* 56, $CDCl_3$) was used. Work-up as before afforded a 65:35 mixture of (+)-*cis*-2-bromo-3-methoxy- and *cis*-1-bromo-4-methoxycyclononene with $[\alpha]^{28}D$ +1.00 ± 0.05° (*c* 91, $CHCl_3$).

**Addition of Bromine to (±)-1,2-Cyclononadiene in Methanol.** A 200-ml three-necked round-bottomed flask was charged with 4.10 g (0.0336 mol) of freshly distilled (±)-1,2-cyclononadiene dissolved in 100 ml of anhydrous methanol, and the magnetically stirred solution was purged with a slow stream of nitrogen. The solution was cooled to 0° with ice, and 5.38 g (0.0336 mol) of bromine in 75 ml of methanol was added in darkness through a dropping funnel over 30 min. The reaction mixture was stirred for an additional 5 min, and then taken up in 100 ml of ether and washed twice with aqueous 10% $NaHCO_3$ (50 ml), followed by five washings with distilled water (50 ml). The ethereal solution was dried over $MgSO_4$ and filtered, and the solvent was removed by rotary evaporation to yield 8.24 g of a slightly yellow oil. Analysis of the crude oil by nmr and glpc (columns as above) revealed a 68:32 mixture of *cis*-1-bromo-4-methoxy- and *cis*-2-bromo-3-methoxycyclononene, respectively. They were spectrally identical with **7** and **8** obtained *via* methanolysis of **5** and **6**; the minor product was spectrally identical with *cis*-2-bromo-3-methoxycyclonene prepared *via* methoxymercuration of **1**, and to authentic **8** reported elsewhere.[16] The oil was distilled *in vacuo* (65–68° (0.05 mm)) to yield 5.6 g (68%) of a mixture of **7** and **8** free from unreacted **1**. About 1.6 g of forerun (45–55° (0.05 mm)) was analyzed by nmr and found to be a 1:1 mixture of the decomposition products **9** and **10**. A higher boiling fraction (1.0 g, 70–90° (0.05 mm)) was found by nmr to be a mixture of the dibromides **5** and **6**, in addition to some **7** and **8**.

**Preparation of *cis*-2-Chloromercuri-3-methoxycyclononene.** To 25 ml of absolute methanol was added 3.19 g (0.01 mol) of mercuric acetate, and the resulting suspension was stirred until solution was nearly complete. To the stirred solution was added 1.22 g (0.01 mol) of (±)-1,2-cyclononadiene in 10 ml of anhydrous methanol. After 5 min of stirring, the reaction mixture showed the absence of $Hg^{2+}$, as evidenced by the absence of yellow $HgCO_3$ upon addition of $Na_2CO_3$. Additional sodium carbonate (1.06 g, 0.01 mol) was added to neutralize acetic acid. The solution was filtered, methanol was removed by rotary evaporation, and the residual oil was extracted away from the inorganic residue with 50 ml of ether. The ether was removed at reduced pressure and the resulting oil was shaken with 10 ml of distilled water. To the oily suspension was added 1.59 g (0.015 mol) of sodium chloride in 10 ml of distilled water and the resultant mixture was shaken vigorously for several minutes; a white crystalline material precipitated immediately. The mercurial was extracted from residual salt with 50 ml of ether. The ether was removed and furnished 2.75 g of a white solid (94%). Recrystallization from 50% aqueous ethanol furnished 2.3 g of fine white needles, mp 111.5–112.5°. A 20% solution of the mercurial in $CDCl_3$ gave the following nmr spectrum: δ 5.76 (t, 1, vinyl), 4.3 (m, 1, methine), 3.28 (s, 3, *O*-methyl), 1.7 (m,

(22) L. Skattebøl and S. Solomon, *Org. Syn.*, **49**, 35 (1969).
(23) See also W. L. Waters, *J. Org. Chem.*, **36**, 1569 (1971).
(24) Our (−)-α-pinene (Aldrich Chemical Co.) showed $[\alpha]^{28}D$ −47.01 ± 0.05° (neat). Optically pure (+)-α-pinene shows $[\alpha]D$ +51.1° (neat). See F. H. Thurber and R. C. Thielke, *J. Amer. Chem. Soc.*, **53**, 1030 (1931).

4, allylic), 1.5 (m, 8, methylene). The spectrum and melting point were identical with authentic mercurial.[25]

**Bromination of *cis*-2-Chloromercuri-3-methoxycyclononene in Carbon Tetrachloride.** *cis*-2-Chloromercuri-3-methoxycyclononene (2.9 g, 0.01 mol) was dissolved in 30 ml of carbon tetrachloride, and 1.60 g (0.01 mol) of bromine in 10 ml of carbon tetrachloride was added dropwise with stirring. The color of bromine was gradually discharged. The reaction mixture was washed three times with water (25 ml), dried over $MgSO_4$, and filtered, and the solvent was removed by evaporation. The residual oil was extracted from inorganic residue with 50 ml of ether, which was subsequently removed at reduced pressure to give 1.7 g of a cloudy oil (73%). The *cis*-2-bromo-3-methoxycyclononene thus prepared was spectrally identical (nmr, glpc) with the product of methanolysis of **6**, with the minor product of bromination of **1** in methanol, and with authentic **8**.[16]

**Addition of Bromine to (*R*)-(+)-1,2-Cyclononadiene in Methanol.** The procedure followed was exactly the same as described for racemic **1**, except that (*R*)-(+)-**1** with $[\alpha]^{28}D$ +23.40 ± 0.05° (neat) was used. The crude oil showed the usual product distribution by glpc and nmr and had $[\alpha]^{28}D$ +7.18 ± 0.05° (neat). The oil was fractionally distilled through a 10-cm Vigreux column to afford three fractions. Fraction one (0.9 g, 40–48° (0.05 mm)) was found by nmr and glpc to consist of 62% **9** and **10**, 38% **7** and **8**; no rotation measurement was taken. The second fraction (6.5 g, 63–69° (0.05 mm)) was found by nmr and glpc to consist of a 95% pure mixture of the methyl ethers **7** and **8** in a respective ratio of 68:32. This fraction showed $[\alpha]^{28}D$ +7.96 ± 0.2° (neat). The third fraction (1.0 g, 75–88° (0.05 mm)) was found by nmr and glpc to be a 1:1 mixture of the dibromides **5** and **6** (62%) and the rest a 9:1 mixture of **7** and **8**, respectively. It showed $[\alpha]^{28}D$ +12.92 ± 0.05° (*c* 40, $CHCl_3$). Fraction two was reexamined as a solution in chloroform, since it was quite colored (neat); it showed $[\alpha]^{28}D$ +7.96 ± 0.05° (*c* 41, $CHCl_3$). The two isomeric bromo ethers were isolated pure *via* preparative glpc using a 20 ft × 3/8 in. aluminum column packed with 20% DC-550 on Chromosorb W (AW, DMCS, 45–60) at 180°. The sample of pure *cis*-1-bromo-4-methoxycyclononene had $[\alpha]^{28}D$ +6.26 ± 0.05° (*c* 10, $CHCl_3$); the sample of *cis*-2-bromo-3-methoxycyclononene showed $[\alpha]^{28}D$ +6.2 ± 0.2° (*c* 12, $CHCl_3$). Reinjected analytically, the 2,3 isomer was found to be contaminated with 9% of the 1,4 isomer.

**Reduction of (+)-*cis*-2-Bromo-3-methoxy- and (+)-*cis*-1-Bromo-4-methoxycyclononene.** About 150 ml of anhydrous ammonia was condensed at −78° into a 500-ml three-necked flask equipped with magnetic stirrer, addition funnel, and Dry Ice condenser. Sodium (4.0 g, 0.174 mol) was added quickly and the resulting dark blue solution was stirred until dissolution was complete (about 10 min). The addition funnel was charged with 4.6 g (0.0197 mol) of a 70:30 mixture of (+)-**7** and (+)-**8**, respectively, in 150 ml of dry pentane. Isolation by preparative glpc prior to reduction showed **8** to have $[\alpha]^{26}D$ +6.8 ± 0.2° (*c* 9, $CHCl_3$) and **7** to have $[\alpha]^{26}D$ +5.9 ± 0.2° (*c* 18, $CHCl_3$). The mixture of **7** and **8** was added dropwise over 40 min to the stirred ammonia kept at −30 to −40° by Dry Ice–isopropyl alcohol. After stirring for an additional hour at −30°, the reaction mixture was quenched by dropwise addition of 100 ml of 10% aqueous $NH_4Cl$. Ammonia was allowed to evaporate at room temperature, 100 ml of ether was added, and the organic layer was washed with four 100-ml portions of distilled water. After drying over $MgSO_4$, solvent was removed by rotary evaporation at reduced pressure to yield 3.4 g of a slightly yellow oil. Analysis by glpc at 165° (using the column described above for separation of **7** and **8**) revealed 71% of the crude product to be a 70:30 mixture of *cis*-4- and *cis*-3-methoxycyclononene (2.45 g, 80% of theory). Collection of the isomerically pure ethers by preparative glpc into weighed collectors revealed that the *cis*-3-methoxycyclononene had $[\alpha]^{26}D$ −2.81 ± 0.05° (*c* 16, $CHCl_3$) and that *cis*-4-methoxycyclononene had $[\alpha]^{26}D$ +2.95 ± 0.05° (neat). The isomeric ethers were characterized on the basis of their nmr spectra. The *cis*-3-methoxycyclononene showed: $\sigma$ 5.1–6.0 (m, 2, vinyl), 4.15 (m, 1, methine), 3.18 (s, 3, $OCH_3$), 1.7–2.5 (m, ~2, allylic), 1.1–1.7 (m, 10, methylene). The *cis*-4-methoxycyclononene had: $\sigma$ 5.1–5.9 (m, 2, vinyl), 3.25 (m, 1, methine), 3.23 (s, 3, $OCH_3$), 1.7–2.7 (m, ~4, allylic), 1.1–1.7 (m, 8, methylene).

(25) W. L. Waters, unpublished results, this laboratory.