921, and 903 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.52 (d of d of d, J = 7.5, 6.0, and 1.5 Hz, CH-6 and CH-7), 4.72 (d, 2, J = 6.0 Hz, CH-5 and CH-8), 3.97 (d of d, 1, J = 5.0 and 8.5 Hz, CH_a-10), 3.58 (d, 1, J = 8.5 Hz, CHb-10), and 2.3 (m, 4, CH-1, CH-2, CH-4, and CH-4a); *m/e* 190.0993 (25) (calcd for $C_{12}H_{14}O_2$, 190.0994), 162 (55), 149 (15), 132 (15), 121 (20), 107 (35), 94 (30), 91 (40), 81 (35), 79 (100), 77 (40), and 66 (30).

6-*exo*-(2-Furyl)hexahydro-3,5-methano-2*H*-cyclopenta[*b*]furan (45) was isolated as a colorless liquid: ν_{max} (CCl_4) 3121, 2965, 2873, 1585, 1500, 1283, 1148, 1080, 1059, 1022, 1011, 957, and 942 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.32 (m, 1, ArH-5'), 6.30 (d of d, 1, J = 3.1 and 1.9 Hz, ArH-4'), 6.00 (d, 1, J = 3.1 Hz, ArH-3'), 4.48 (d, 1, J = 5.0 Hz, CH-6a), 3.92 (d of d, 1, J = 8.1 and 4.2 Hz, CH_a-2), and 3.76 (d, 1, J = 8.1 Hz, CHb-2); *m/e* 190.0996 (50) (calcd for $C_{12}H_{14}O_2$, 190.0994), 132 (100), 94 (40), 91 (45), 81 (60), 79 (75), 77 (60), and 69 (30).

6a-(2-Furyl)hexahydro-3,5-methano-2*H*-cyclopenta[*b*]furan (46) was isolated as a colorless liquid: ν_{max} (CCl_4) 2968, 2873, 1325, 1292, 1156, 1140, 1074, 1003, and 908 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.39 (br, 1, ArH-5'), 6.33 (d of d, 1, J = 2.0 and 3.0 Hz, ArH-4'), 6.23 (d, 1, J = 3.0 Hz, ArH-3'), 4.04 (d of d, 1, J = 4.2 and 8.0 Hz, CH_a-2), and 3.76 (d, 1, J = 8.0 Hz, CH_b-2); *m/e* 190.0996 (65) (calcd for $C_{12}H_{14}O_2$, 190.0994), 161 (100), 160 (85), 147 (25), 135 (30), 95 (90), 91 (35), 81 (25), 79 (35), and 77 (35).

Irradiation of 6-*exo*-Iodohexahydro-3,5-methano-2*H*-cyclopenta[*b*]-furan-2-one (48). A solution of 265 mg of iodolactone **48**[14] in 20 mL of methanol was irradiated for 4 h at 254 nm. The results are summarized in Scheme VIII. Removal of solvent by distillation, followed by isolation using preparative gas chromatography, afforded the following products:

Hexahydro-3,5-methano-2*H*-cyclopenta[*b*]furan-2-one (50) was obtained as a waxy, colorless solid that was identical in every respect with an authentic specimen.[15]

8-Oxatetracyclo[4.3.0.0^{2,4}.0^{3,7}]nonan-9-one (51) was obtained (A) as a colorless oil: λ_{max} 3075, 3010, 1800, 1337, 1308, 1149, 1010, 1000, 992 and 978 cm^{-1}; ^{1}H NMR τ 5.33 (m, 1), 7.42 (br s, 2), and 8.24 (s, 5); *m/e* 136.0508 (22) (calcd for $C_8H_8O_2$, 136.0524), 92 (60), 91 (100), 79 (52), 77 (26), and 66 (34).

3,3a,6,6a-Tetrahydro-3,6-methano-2*H*-cyclopenta[*b*]furan-2-one (52) was obtained (B) as a colorless oil: ν_{max} 3080, 1800, 1332, 1173, 1027, 1000, 748 and 718 cm^{-1}; ^{1}H NMR τ 3.68 and 4.33 (2m, 2, CH-4 and -5), 5.73 (br s, 1, CH-6a), 6.81 (m, 1, CH-6), 7.25 (m, 1, CH-3a), 7.63 (br d, J = 7.0 Hz, 1, CH-3), 8.20 and 8.73 (2d of d, J = 10.5 and 5.0 Hz, 2, CH_2-7); *m/e* 136.0523 (4) (calcd for $C_8H_8O_2$, 136.0524), 92 (25), 79 (100), and 77 (27).

6-*exo*-Methoxyhexahydro-3,5-methano-2*H*-cyclopenta[*b*]furan-2-one (54) was obtained as a colorless liquid having an infrared spectrum identical with that of a sample prepared independently as described below: ν_{max} (CCl_4) 1791, 1339, 1176, 1130, 1098, 1038, and 1019 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.28 (d, 1, J = 5.0 Hz, CH-6a), 3.36 (s, 3, $-OCH_3$), 3.2 (m, 2, CH-3 and CH-6), and 2.5 (m, 2, CH-3a and CH-5); *m/e* 168.0784 (30) (calcd for $C_9H_{12}O_3$, 168.0786), 140 (35), 80 (35), and 71 (100).

5-*exo*-Methoxyhexahydro-3,6-methano-2*H*-cyclopenta[*b*]furan-2-one (55) was obtained as a colorless liquid: ν_{max} (CCl_4) 1792, 1342, 1307, 1213, 1162, 1131, 1107, 1028, 1004, 951, and 931 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.96 (br, 1, CH-6a), 3.53 (d, 1, J = 6.0 Hz, CH-5), 3.29 (s, 3, $-OCH_3$), and 2.66 (m, 3, CH-3, CH-3a, and CH-6); *m/e* 168.0784 (calcd for $C_9H_{12}O_3$, 168.0786), 136 (60), 108 (40), 92 (55), 80 (50), 79 (100), and 66 (30).

Independent Synthesis of Lactone 54. A solution of 155 mg (1.01 mmol) of ether **27** in 10 mL of acetone was treated with excess 8 N chromic acid[38] at room temperature under a nitrogen atmosphere.[11] After 10 days of stirring, the green solids were removed by filtration and washed with acetone. The filtrate was dissolved in 50 mL of ether, and the solution was washed with saturated sodium bicarbonate and saturated sodium chloride solutions and dried over anhydrous sodium sulfate. Removal of the solvent afforded 110 mg of a viscous yellow liquid, which was purified by Kugelrohr distillation at 80–120 °C (0.1 mm) to give 90 mg (54% yield) of lactone **54** as a colorless liquid having an infrared spectrum identical with that of material obtained from irradiation of iodolactone **48** in methanol.

Acknowledgment. Generous financial support by the National Science Foundation, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and by the University of North Carolina Research Council is gratefully acknowledged.

Registry No. 4, 931-98-6; **5**, 280-33-1; **6** (Y = OCH_3), 7697-14-5; **6** (Y = OC_2H_5), 49576-41-2; **7**, 61192-26-5; **8**, 6221-55-2; **9**, 61192-23-2; **10**, 63160-85-0; **11**, 280-65-9; **12**, 63160-90-7; *endo*-**15**, 15507-06-9; *exo*-**15**, 13360-81-1; **16**, 42464-05-1; **16-*d***, 81523-23-1; **17**, 81571-06-4; **19**, 3354-68-5; **20**, 81523-24-2; **23**, 33237-15-9; **24**, 81523-25-3; **25**, 81523-26-4; **26a**, 22532-37-2; **26b**, 81523-27-5; **26b-*d***, 81523-28-6; **27**, 33892-28-3; **28**, 81523-29-7; **29**, 35359-71-8; **30**, 81523-30-0; **32**, 27867-33-0; **33**, 18684-64-5; **34**, 81523-31-1; **34-*d***, 81523-32-2; **35**, 42392-37-0; **36**, 70680-88-5; **37**, 81523-33-3; **38**, 81523-34-4; **39**, 81523-35-5; **40**, 81523-36-6; **41-*d***, 81523-37-7; **42**, 16053-06-8; **42-*d***, 81523-38-8; **43**, 81523-39-9; **44**, 81523-40-2; **45**, 81523-41-3; **46**, 81523-42-4; **48**, 7732-50-5; **50**, 6712-12-5; **51**, 6169-95-5; **52**, 81523-43-5; **54**, 81523-44-6; **55**, 81523-45-7; bicyclo[3.2.1]octane-1-carboxylic acid, 2534-83-0; 1-(methoxycarbonyl)bicyclo[3.2.1]octane, 81523-46-8; 1-(ethoxycarbonyl)bicyclo[3.2.1]octane, 81523-47-9; methyl 6-oxonorbornan-2-*endo*-carboxylate 6-ethylene ketal, 70600-43-∞0.

(38) Bowden, H.; Heilbron, J. M.; Jones, E.; Weedon, B. *J. Chem. Soc.* **1946**, 39.

Stereospecificity of the Oxymetalation of Optically Active 1,2-Cyclononadiene

Robert D. Bach,* Joseph W. Holubka, and Carl L. Willis

Contribution from the Department of Chemistry, Wayne State University, Detroit, Michigan 48202. *Received November 16, 1981*

Abstract: The absolute configuration of (−)-1,2-cyclononadiene was established as *S*. The absolute configurations of (+)-(*Z*)-3-hydroxy-, alkoxy-, and acetoxycyclononene were assigned the *S* configuration on the basis of the silver ion induced solvolysis of optically active 9,9-dibromo-(*E*)-bicyclo[6.1.0]nonane of known stereochemistry. The stereospecificity of antarafacial oxymercuration and oxythallation of (−)-1,2-cyclononadiene has been determined by NMR techniques to be a function of the ligand on the metal. The stereospecificity of suprafacial acetoxyplumbation of (−)-1,2-cyclononadiene was shown to be 56%.

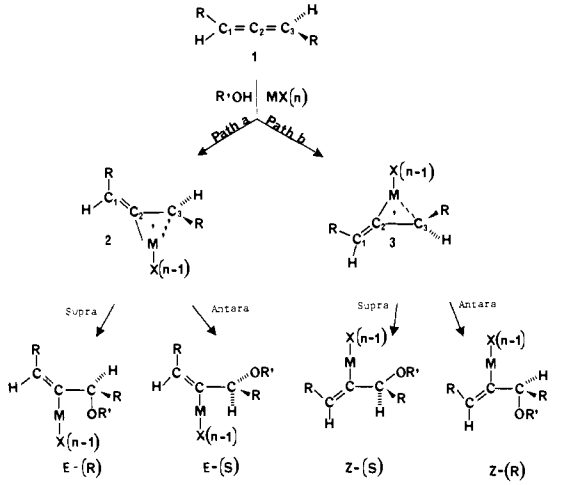
The generally accepted mechanism for the oxymercuration of an alkene involves a bridged or π-complexed mercurinium ion intermediate.[1] This reaction was initially extended to include allenes by Gardner, who elucidated the structures of the oxymercurials derived from addition of mercuric acetate to 1,2-cyclononadiene, to 1,2,6-cyclononatriene, and to 2,3-pentadiene in ethanol.[2] Waters and Kiefer invoked the intermediacy of a σ-bridged intermediate in the methoxymercuration of a series of

(1) (a) Kitching, W. *Organomet. Chem. Rev., Sect. A* **1968**, *61*. (b) Kitching, W. *Organomet. React.* **1972**, *3*, pp 319–98.

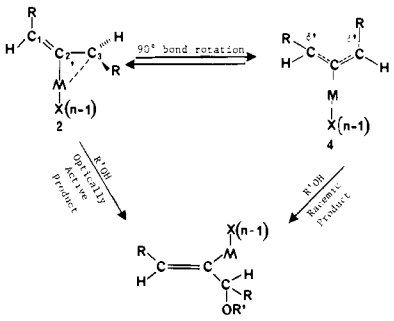
(2) Sharma, R. K.; Shoulders, B. A.; Gardner, P. D. *J. Org. Chem.* **1967**, *32*, 241. Pasto, D. J.; Miles, M. F. *Ibid.* **1976**, *41*, 425.

0002-7863/82/1504-3980$01.25/0

Scheme I



Scheme II



methyl-substituted allenes.[3] Optically active 2,3-pentadiene[4] and 1,2-cyclononadiene[5] were subsequently utilized in mechanistic studies in an effort to determine the relative stereospecificity of solvent addition and to provide evidence for a mercurinium ion intermediate. Chiral allenes have also been used as mechanistic probes in the related oxythallation[6] and oxyplumbation[7,8] reactions.

The oxymetalation of a symmetrically disubstituted allene is regiospecific and affords an organometallic with the metal bonded to the central sp carbon of the allenic moiety with nucleophilic attack of the solvent or the ligand on the metal at the terminal (C_1 or C_3) carbon (Scheme I). In principle, four stereoisomers may arise by both supra- and antarafacial addition to the two enantiotopic faces of the identical double bonds. With an acyclic allene such as **1** there are two possible directions of attack for the electrophilic metal. The least hindered pathway involves formation of π complex **2** by an approach that is parallel to the hydrogen on the adjacent mutually orthogonal double bond (path a). However, examination of molecular models suggests that this complex, if nonlinear as inferred in **2**, will have potential alkyl–alkyl steric interactions. In contrast, the alternate pathway (path b) affording **3** is initially hindered by the alkyl substituent at the vinyl terminus (C_1) but ultimately affords a nonlinear complex that is actually less sterically crowded having only hydrogen–alkyl interactions.[4,7b] In a detailed study of the oxymercuration of (*R*)-(−)-1,3-dimethylallene, Caserio[4] observed an 83:17 ratio of *Z*:*E* stereoisomers, with path b dominating. We presented[7b] a similar steric argument in explanation of the stereochemical course of the oxyplumbation of this allene.

The use of an optically active allene provides a practical method for determining the preferred mode of electrophilic addition to an allenic double bond. If the absolute configuration of the allene and the product of oxymetalation can be adduced, then the minimum stereospecificity and the ratio of supra- vs. antarafacial addition to either **2** or **3** will be reflected in the optical yield of the reaction. If a bridged intermediate is involved and the addition reaction is stereospecific, then a single enantiomer will result from either pathway (Scheme I). However, the overall mechanistic analysis is further complicated by the dynamic equilibrium between the bridged π complex and its open cation (Scheme II).[5] Since the orbitals required for π-complex formation 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 carbenium ion **4** by a 90° rotation about the C_2–C_3 bond in **2** (or **3**). If cation **4** attains planarity prior to the attack by solvent, then a racemic product will result and the optical purity of the product will be a consequence of the supra- vs. antarafacial addition, as well as the partition between **2** and **4**. Obviously, reversion to **2** (or **3**) is tantamount to racemization and will produce an achiral mercurinium ion intermediate.

In an earlier paper we found that the stereospecificity of oxymercuration of optically active 1,2-cyclononadiene (**5**) was related to the ionic nature of the mercuric salt employed.[5] The chemical similarity between the electrophilic nature of the isoelectronic mercury(II), thallium(III), and lead(IV) reagents has been recognized for some time. However, the lack of stability of the resulting organothallium and organolead adducts formed in these reactions has limited mechanistic studies on these oxymetalation reactions. We now report the absolute configuration and optical purities of the products derived from oxymetalation of optically active **5** with Hg^{II}, Tl^{III}, and Pb^{IV} metal salts. The relative stereospecificity of each of these electrophilic addition reactions has been determined.

Results and Discussion

We chose 1,2-cyclononadiene as our model substrate because its oxymetalation can only afford two of the possible four stereoisomers, which greatly simplifies the mechanistic interpretation. Examination of this cyclic allene reveals that the two double bonds are identical (C_2 symmetry) and that one enantiotopic face of each double bond is not readily accessible to electrophilic attack. The time-averaged conformation of the mobile methylene chain severely hinders π-complex formation "inside" the ring. This geometric constraint effectively precludes pathway b (Scheme I) and can potentially only afford the two enantiomeric *E* stereoisomers (containing the cis double bond). When the size of the ring is increased to 13 carbon atoms, then both pathways are accessible and the *Z* isomer is also observed.[5,9] Oxymercuration of medium-ring allenes containing additional unsaturation affords rearrangement products arising from transannular π-bond interactions.[10]

1,2-Cyclononadiene (**5**) of high optical purity may be obtained from optically pure *trans*-cyclooctene (**6**). Treatment of **6**, $[\alpha]^{25}_D$ +440°, with $CHBr_3$ and potassium *tert*-butoxide results in the formation of (1*R*,8*R*)-(−)-9,9-dibromo-*trans*-bicyclo[6.1.0]nonane (**7**). The methyllithium-induced α elimination of **7** has afforded (*S*)-(−)-1,2-cyclononadiene with an observed rotation as high as −166° (*c* 1.4, CH_2Cl_2).[11,12] One serious drawback of this preparation of 1,2-cyclononadiene is the difficulty in obtaining *trans*-cyclooctene of high optical purity. 1,2-Cyclononadiene of lower enantiomeric purity, $[\alpha]^{25}_D$ −22.9°, may be obtained by a

(3) Waters, W. L.; Kiefer, E. F. *J. Am. Chem. Soc.* **1967**, *89*, 6261.
(4) Waters, W. L.; Linn, W. S.; Caserio, M. C. *J. Am. Chem. Soc.* **1968**, *90*, 6741.
(5) (a) Bach, R. D. *Tetrahedron Lett.* **1968**, 5841. (b) Bach, R. D. *J. Am. Chem. Soc.* **1969**, *91*, 1771.
(6) Bach, R. D.; Holubka, J. W. *J. Am. Chem. Soc.* **1974**, *96*, 7814.
(7) (a) Bach, R. D.; Mazur, U.; Brummel, R.; Lin, L. H. *J. Am. Chem. Soc.* **1971**, *93*, 7120. (b) Bach, R. D.; Brummel, R. N.; Holubka, J. W. *J. Org. Chem.* **1975**, *40*, 2559.
(8) In an earlier study the major product of the reaction of acyclic allenes with lead tetraacetate was reported to be a diacetate. Laforge, F. B.; Acree, F. *J. Org. Chem.* **1941**, *6*, 208.
(9) Vaidyanathaswamy, R.; Devaprabhakara, D. *Tetrahedron Lett.* **1971**, 915. Joshi, G. C.; Devaprabhakara, D. *J. Organomet. Chem.* **1968**, *15*, 497.
(10) Thies, R. W.; Hong, P.-K.; Buswell, R.; Boop, J. L. *J. Org. Chem.* **1975**, *40*, 585. Theis, R. W.; Hong, P.-K.; Buswell, R. *J. Chem. Soc., Chem. Commun.* **1972**, 1091.
(11) Moore, W. R.; Bach, R. D. *J. Am. Chem. Soc.* **1972**, *94*, 3148.
(12) Cope, A. C.; Moore, W. R.; Bach, R. D.; Winkler, H. J. S. *J. Am. Chem. Soc.* **1970**, *92*, 1243.

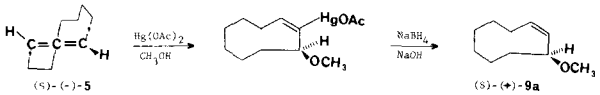
Table I. Optical Rotations[a] on Products of Silver-Catalyzed Rearrangements of 7

compd	solvent	rotation of 7, deg	obsd rotation, deg	calcd absolute rotation,[b] deg	opt purity from % solvol	[(E) − 10]/[(Z) − 11]
10a	CH_3OH	−43.7	+44.5	98.4	43.9	92:8
9a			−13.1[c]	30.8 (30.5)		
10b	C_2H_5OH	−43.7	36.0	89.3	40.2	95:5
9b			−20.2[c]	50.6		
10c	CH_3COOH	45.2	−7.1	36.0	19.7	100:0
9c				−76.2[d]		

[a] Specific rotations measured in CH_2Cl_2 solution at 25 °C. [b] Absolute rotation is synonymous with the rotation of the pure enantiomer. [c] Observed rotation of the product derived from $Na/NH_3(l)$ reduction of the corresponding vinyl bromide. [d] Calculated from 9c, obtained from reduction of propargyl acetate.

kinetic resolution[4] using the chiral borane tetraisopinocamphenyldiborane.[13] Since the maximum observed rotation of **5** has been estimated to be 175°,[14] the optical yield of this reaction is approximately 13%.

Stereochemistry of the Products of Oxymetalation. Oxymercuration of 1,2-cyclononadiene (**5**) affords 3-methoxy-(*Z*)-cyclononene (**9a**) after demetalation[5] (eq 1). The overall ster-



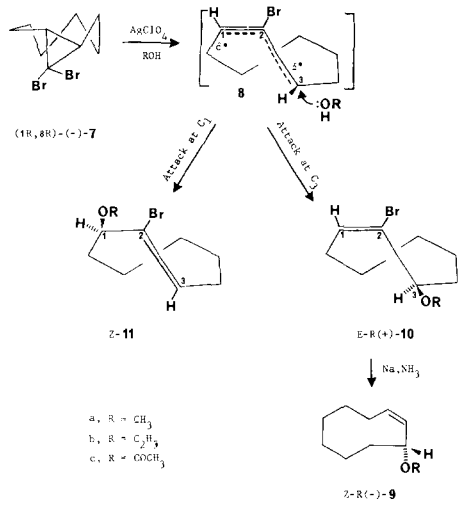
(1)

eochemistry of electrophilic addition was found to be similar in either methanol or acetic acid solvent. The assignment of an absolute configuration to **9** and its related compounds is based upon its chemical correlation with optically pure 9,9-dibromo-*trans*-bicyclo[6.1.0]nonane (**7**) of known stereochemistry.[15] The (−) enantiomer of *trans*-cyclooctene afforded **7**, $[\alpha]^{25}_D$ +44.2° (*c* 2.49, CH_2Cl_2). An X-ray study[15,16] on tetragonal crystals of **7** showed this compound to exist in a distorted crown conformation. This structure established the absolute configuration of (+)-(1*S*,8*S*)-**7** and corroborated the assignment[17] of the absolute stereochemistry of (−)-*trans*-cyclooctene as *R*.

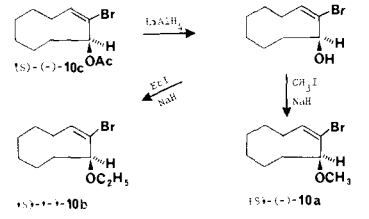
The silver perchlorate induced ring expansion of **7**, $[\alpha]^{25}_D$ −43.7°, in methanol solvent afforded 2-bromo-3-methoxycyclononene (**10a**), $[\alpha]^{25}_D$ +44.5°, in essentially quantitative yield after a 10-min reaction time at room temperature. Reduction of **10a** with sodium in liquid ammonia afforded **9a**, $[\alpha]^{25}_D$ −13.1° (Scheme III). The methyl ether **9a** was in every respect identical with the sample prepared from methoxymercuration of 1,2-cyclononadiene (eq 1). The cyclopropyl–allyl transformation with **7** in anhydrous ethanol required 4 h and gave **10b**, $[\alpha]^{25}_D$ +36.0° (92%). Similarly, reduction of **10b** afforded the *Z* ethyl ether **9b**, $[\alpha]^{25}_D$ −20.2°. Acetolysis of optically pure **7**, $[\alpha]^{25}_D$ +45.2°, with excess $AgClO_4$ in glacial acetic acid for 30 min resulted in 80% conversion to the *cis*-acetate **10c**, $[\alpha]^{25}_D$ −7.1°.

Isolation of optically active products from the silver-catalyzed solvolysis of **7** precludes a long-lived achiral carbenium ion as the sole intermediate. The rate of racemization of **10a–c** under the reaction conditions is too slow to account for the observed loss of optical activity (vide infra) so a concerted solvolysis of **7** may be excluded. We, therefore, conclude that the retention of optical activity arises by preferential attack by solvent on the chiral carbenium ion **8** from the least hindered face of the delocalized allylic cation. Examination of molecular models clearly indicates that the developing cation is more accessible to attack from "outside" the ring since the opposite approach is effectively shielded by the methylene chain that comprises the ring. Since **7** has C_{2v} symmetry, (*R*)-(+)-**10** would be formed regardless of which of

Scheme III



Scheme IV



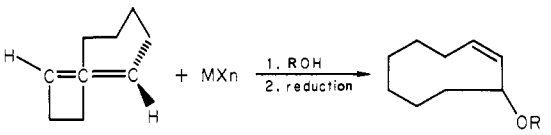
the two asymmetric centers in **7** (C-1 or C-8) becomes the allylic site in **10**.

Orbital symmetry considerations predict that the silver ion promoted ring expansion of the *trans*-dibromocarbene adduct **7** would proceed by a disrotatory process affording the *cis,trans*-allyl cation **8**. Attack by solvent on C_1 would afford the *trans*-vinyl bromide **11**, while attack at C_3 would result in the cis isomer **10** (Scheme III). In all three cases the observed stereospecificity was greater than 90%, with the thermodynamically more stable *E* isomer predominating (Table I). The optical stability of **8** derives from the steric inhibition to free rotation of the methylene chain. Racemization of **8** requires rotation of the planar allyl moiety through the ring until a symmetry plane is achieved. Since the strained *trans,trans*-allyl cation derived from 9,9-bromo-*cis*-bicyclo[6.1.0]nonane maintained its stereochemical integrity upon solvolysis,[18] in all probability the allyl group in **8** does not undergo isomerization.

The enantiomeric purity of **10c** was determined through the use of the chiral shift reagent Eu-Opt according to an established NMR procedure.[19] The acetate resonance of the *S* enantiomer was observed at δ 3.98 and the *R* stereoisomer had a singlet at δ 3.86. A sample of **10c** having $[\alpha]^{25}_D$ −8.5° exhibited acetate resonances in a ratio of 38.2:61.8, which is consistent with a

(13) Brown, H. C.; Ayyangar, N. A.; Zweifel, G. *J. Am. Chem. Soc.* **1964**, *86*, 397. *Ibid.* **1964**, *86*, 1071.
(14) Moore, W. R.; Bach, R. D.; Ozretich, T. M. *J. Am. Chem. Soc.* **1969**, *91*, 5918.
(15) Bach, R. D.; Mazur, W.; Hamama, I.; Lauderback, S. K. *Tetrahedron* **1972**, *28*, 1955.
(16) We are indebted to Drs. S. H. Simonsen and B. J. Bowen for the X-ray analysis. Bowen, B. J. Ph.D. Thesis, University of Texas, Austin, Texas, 1969.
(17) Cope, A. C.; Mehta, A. S. *J. Am. Chem. Soc.* **1964**, *86*, 5626. Manor, P. C.; Shoemaker, D. P.; Parkes, A. S. *Ibid.* **1970**, *92*, 5260.
(18) Reese, C. B.; Shaw, A. *J. Am. Chem. Soc.* **1970**, *92*, 2566.
(19) Goering, H. L.; Elkenberry, J. N.; Koermer, G. S. *J. Am. Chem. Soc.* **1971**, *93*, 5913. Whitesides, G. M.; Lewis, D. W. *Ibid.* **1971**, *93*, 5914.

Table II. Oxymetalation of 1,2-Cyclononadiene



5						9		
$[\alpha]^{25}_D$, deg	% opt purity[a]	MXn	R	reacn time, h	catalyst	$[\alpha]^{25}_D$, deg	% opt purity	stereospecificity of reacn, %
−99.8	57.1	$Pb(OAc)_4$	$C(O)CH_3$	14		−24.6[b]	32.3[c]	56.5
−15.6	8.9	$Tl(OAc)_3$	$C(O)CH_3$	20	$BF_3{\cdot}Et_2O$	+0.6	0.78[c]	8.8
−19.6	11.2	$Tl(OAc)_3$	$C(O)CH_3$	72	$BF_3{\cdot}Et_2O$	+0.45	0.59[c]	5.3
−15.6	8.9	$Tl(OAc)_3$	CH_3	20	$BF_3{\cdot}Et_2O$	+1.89	6.2[d,e]	69.6
−9.1	5.2	$Tl(OAc)_3$	CH_3	72	$BF_3{\cdot}Et_2O$	+1.38	4.5[d,e]	86.5
−15.6	8.9	$Tl(OAc)_3$	CH_2CH_3	20	$BF_3{\cdot}Et_2O$	+2.87	5.67[f]	63.7
−22.7	13.0	$Tl(NO_3)_3$	CH_3	3		+2.19	7.2[d,e]	55.4
−22.7	13.0	$Tl(NO_3)_3$	CH_3	12		+1.17	3.8[d,e]	29.3
−22.7	13.0	$Tl(NO_3)_3$	CH_2CH_3	3		+2.67	5.3[f]	40.8
−22.7	13.0	$Tl(NO_3)_3$	CH_2CH_3	20		+1.14	2.3[f]	17.6
−45.8	26.2	$Hg(OAc)_2$	$C(O)CH_3$	1		+1.08[g]	1.42[c]	5.4
−81.8	46.7	$Hg(OAc)_2$	CH_2CH_3	5	$BF_3{\cdot}Et_2O$	+12.4[h]	24.5[f]	52.5
−81.8	46.7	HgO	CH_3	5	$BF_3{\cdot}Et_2O$	+7.3[h]	23.9[d,e]	51.2
−81.8	46.7	HgO	CH_2CH_3	1	$BF_3{\cdot}Et_2O$	+11.2[h]	22.1[f]	47.3
−81.8	46.7	$Hg(NO_3)_2$	CH_2CH_3	5		+9.9[h]	19.6[f]	41.9
−81.8	46.7	$Hg(ClO_4)_2$	CH_2CH_3	10		+12.1[h]	23.9[f]	51.2

[a] Based on the highest observed rotation of 175° (see ref 14). [b] Product obtained by the reduction of 3-acetoxycyclononyne with $Ni(OAc)_2$ and $NaBH_4$. [c] Based on an absolute rotation of $[\alpha]^{25}_D$ +76.3°. [d] Based on the calculated absolute rotation of $[\alpha]^{25}_D$ +30.54°. [e] A calculated value for absolute rotation for *cis*-3-methoxycyclononene is $[\alpha]^{25}_D$ +30.8°. [f] Reference 5b. [g] Reference 7a. [h] Reference 5a.

rotation of +36.0° for an optically pure sample. The maximum specific rotations of the methyl and ethyl ethers **10a** and **10b** were established as outlined in Scheme IV and the data are summarized in Table I. The methyl and ethyl NMR signals of the respective enantiomers of **10a** and **10b** could not be effectively separated with several chiral shift reagents in the absence of the bromo substituent.

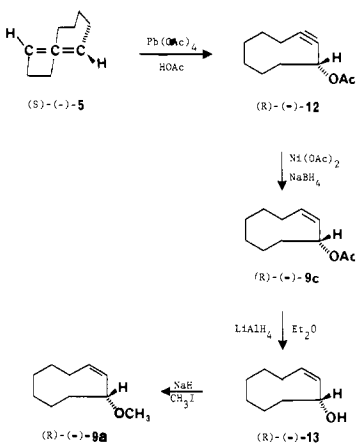
An independent check on the enantiomeric purity and absolute rotation of debromomethyl ether **9a** was achieved by NMR studies on the propargyl acetate **12** (vide infra) obtained from oxyplumbation of (−)-1,2-cyclononadiene (Scheme V). (*S*)-(−)-3-Acetoxycyclononyne (**12**), $[\alpha]^{25}_D$ +49.7°, exhibited one acetate signal for the *R* enantiomer (230 Hz) and another for the *S* enantiomer (240 Hz) in the presence of Eu–Opt. A sample of **12** having $[\alpha]^{25}_D$ +49.3° showed these peaks to be in a ratio of 66:34, which corresponds to an absolute rotation of $[\alpha]^{25}_D$ +154.8° for **12**.

We found that the propargyl acetate **12**, $[\alpha]^{25}_D$ +49.7° (32.3% optically pure), could be efficiently reduced to the allylic acetate **9c**, $[\alpha]^{25}_D$ −24.6°, by hydrogenation in ethanol using a nickel boride catalyst (Scheme V). This observed rotation corresponds to a calculated absolute rotation for (*R*)-*cis*-3-acetoxycyclononene (**9c**) of −76.2°. In a similar manner, 3-hydroxycyclononene (**13**), $[\alpha]^{25}_D$ −15.5°, was obtained from (*R*)-(−)-**9c**, $[\alpha]^{25}_D$ −24.6° (32.3% optical purity), via reduction with lithium aluminum hydride. This value corresponds to a calculated absolute rotation for 3-hydroxycyclononene of $[\alpha]^{25}_D$ +47.9°.

Thus, a second estimate of the absolute rotation of *cis*-3-methoxycyclononene may be made by utilizing **13**, $[\alpha]^{25}_D$ +8.3° (17.4% optically pure), which, upon conversion to 3-methoxycyclononene by the Williamson ether synthesis, had $[\alpha]^{25}_D$ +5.3°. With our calculated absolute rotation for **13**, an optical purity of 17.4% may also be estimated for **9c**, $[\alpha]^{25}_D$ +5.3°. This value is consistent with an absolute rotation of *cis*-3-methoxycyclononene of $[\alpha]^{25}_D$ +30.5°, which is in excellent agreement with the above calculation (Table I).

Stereospecificity of Oxymetalation. The absolute configuration of 1,2-cyclononadiene has been assigned on the basis of an ORD–CD correlation[20] and chemically by relating the stereochemistry of the products of lead tetraacetate (LTA) oxidation (Scheme V) and oxymercuration (eq 1) of (−)-1,2-cyclononadiene to the *cis*-3-alkoxycyclononenes obtained by the silver-induced rearrangement of the *trans*-dibromide **7** (Scheme III).[7a] This series of reactions established that acetoxy-, alkoxy-, and hydroxymercuration of (−)-1,2-cyclononadiene all occur principally by an antarafacial addition, with the topology of the reaction such that electrophilic attack by HgX_2 occurs from "outside" the ring. However, oxyplumbation with LTA in acetic acid proceeded by a suprafacial addition to the allenic double bond. This is compelling evidence that the (−)-1,2-cyclononadiene must have the *S* configuration in order for the latter reaction to afford (−)-**9c** with the *R* configuration (Scheme V). This syn mode of addition was corroborated by a similar study on the stereochemistry of the oxyplumbation of (+)-1,3-dimethylallene.[7b]

Scheme V

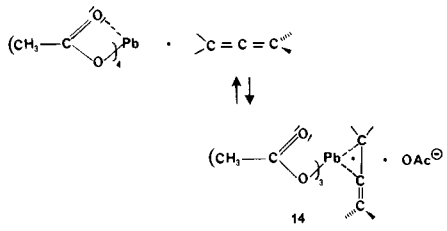


The overall stereospecificity of oxymetalation of (−)-**5** was determined by relating the optical purity of the starting allene to that of the resulting allylic product as described above. The results tabulated in Table II show that acetoxyplumbation proceeded with a net 56% suprafacial addition. Thus, treatment of (−)-**5**, $[\alpha]^{25}_D$ −99.8°, with LTA in glacial acetic acid afforded (*R*)-(+)-3-acetoxycyclononyne (**12**), $[\alpha]^{25}_D$ +50.2°. An average optical purity of 32.3% was observed, which corresponds to an

(20) Moore, W. R.; Anderson, H. W.; Clark, S. D.; Ozretich, T. M. *J. Am. Chem. Soc.* **1971**, *93*, 4932.

overall stereospecificity of addition of approximately 56% since the estimated optical purity of the starting allene was 57%.

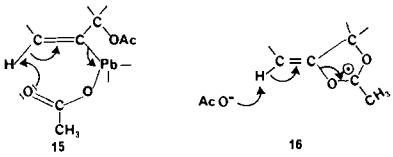
The stereospecificity of suprafacial acetoxyplumbation of (−)-**5** is quite high in comparison to the corresponding antarafacial acetoxythallation (8.8%) and acetoxymercuration (5.4%) reactions. This difference in mechanism and reactivity may be attributed to the manner in which the ligands are bound to the metal ion. Spectroscopic studies have indicated that the four acetoxy ligands on LTA are coordinated to the lead in an octahedral complex where the carbonyl oxygens are also metal bound.[21] Donor ligands such as pyridine displace an acetate anion from LTA to form a complex.[21a] By analogy, we suggest the π bond of an allene can form a similar complex in acetic acid solution (eq 2). Once π



(2)

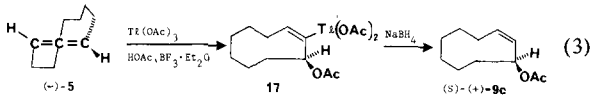
complexation has been achieved, the bulky three-dimensional nature of **14** should greatly facilitate suprafacial intramolecular delivery of the acetate ion. In addition, the relatively high charge on the metal ion should increase its reactivity and strongly perturb the π system, facilitating the nucleophilic addition of acetate anion.

The relative stability of the vinyl carbon–metal bond, where C–Hg > C–Tl ≫ C–Pb, also influences the reaction pathway. In the latter case, reductive cleavage of the carbon–lead bond occurs in situ and an alkyne is produced. We suggest[7b] that this may occur either by an intramolecular syn elimination as depicted in **15** or by prior ionization of the labile C–Pb bond with formation of acetoxonium ion **16**.



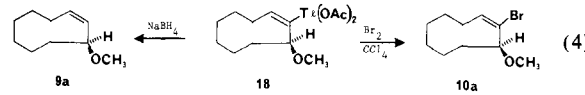
Organometallic compounds containing the carbon–thallium bond are also generally labile and their isolation has been hindered. As a result, only a few compounds have been isolated in the oxythallation reaction of alkenes.[22] We anticipated that the thallium adduct derived from an allene would potentially be more stable since heterolysis of the carbon–thallium bond would afford a relatively unstable vinyl cation.

In a typical oxythallation reaction, treatment of (−)-**5**, $[\alpha]^{25}_{D}$ −15.6°, with an equivalent of $Tl(OAc)_3$ and a catalytic amount of boron trifluoride etherate in glacial acetic acid afforded the thallium adduct **17** (84%), which gave (*S*)-(+)-(*Z*)-3-acetoxycyclononene (**9c**) upon reduction with sodium borohydride (eq 3).



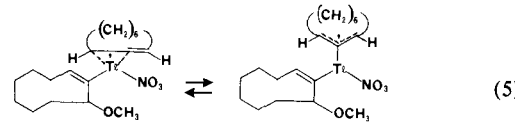
(3)

The reaction of (−)-1,2-cyclononadiene with $Tl(OAc)_3$ in methanol also afforded a stable methoxythallium adduct **18**, with the expected regiochemistry. Demetalation of **18** with $NaBH_4$ afforded (*S*)-(+)-(*Z*)-3-methoxycyclononene (**9a**). The structure of the (diacetato)thallium adduct **18** was confirmed by bromination in CCl_4 solution to afford *cis*-2-bromo-3-methoxycyclononene (**10a**) (eq 4). The methoxythallation of (−)-**5** with $Tl(OAc)_3$ proceeded by greater than 70% antarafacial addition, and the stereospecificity did not decrease as the reaction time was increased (Table II).



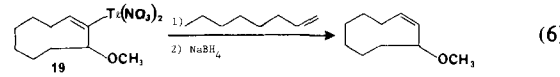
(4)

Oxythallation of (−)-**5** with $Tl(NO_3)_3$ in alcoholic solvents failed to afford (dinitrato)thallium adducts that could be characterized. We also observed that products of lower optical purity were obtained when reaction times were increased. Control experiments established that (−)-**5** was not racemized by the mole of HNO_3 liberated on oxymetalation of the double bond. We also excluded reversible oxymetalation (Scheme II) involving the achiral planar allylic cation **4**. Treatment of the (diacetato)thallium adduct **18** with HNO_3 in ethanol failed to result in alkoxy exchange as has been observed in the oxymercuration reaction.[23] The allene (−)-**5** is also optically stable in a methanolic solution of the (diacetato)thallium adduct **18**. However, a solution containing (−)-**5**, $[\alpha]^{25}_{D}$ −15.2°, was completely racemized in the presence of racemic 2-[(dinitrato)thallio]-3-methoxycyclononene (**19**) in 3 h. Thus, we conclude that the relatively ionic **19** is sufficiently electrophilic to racemize the allene during the course of the reaction. Ionization of **19** and reversible π complexation with (−)-**5** provide a rationale for the above observations (eq 5).



(5)

We also found that **19** would rapidly isomerize the highly strained alkene *trans*-cyclooctene without metalation of the double bond, presumably by a comparable process. Consistent with this observation, treatment of **19** with 1-octene in methanol failed to result in alkene exchange[23b] (eq 6). Failure to detect any products



(6)

derived from oxythallation of 1-octene upon $NaBH_4$ reduction of this reaction mixture suggests that the thallium adduct **19** is not formed reversibly and that allene racemization cannot be attributed to the reversible equilibrium generalized in Scheme II.

The stereospecificity of antarafacial alkoxymercuration of (−)-**5** with a series of mercuric salts at room temperature falls in the range 42–52%. Interestingly, methoxymercuration of (+)-**5** with $Hg(OAc)_2$ has been reported by Pirkle[24] on the basis of an NMR study to be 78% stereospecific at −78 °C. In our previous study we reported the highest stereospecificity (65%) for ethoxymercuration using ethylmercuric acetate and the lowest (<1%) with $HgCl_2$. It should be noted that this trend does not reflect the electrophilic or ionic character of the mercuric salt since $Hg(ClO_4)_2$ is highly reactive toward an alkene while EtHgOAc and $HgCl_2$ will not add to an unstrained alkene under normal oxymercuration conditions.

In summary, we have established the absolute configuration of (−)-1,2-cyclononadiene as *S*. The absolute stereochemistry of the series of (*Z*)-(+)-3-acetoxy-, alkoxy-, and hydroxycyclononenes was assigned the *S* configuration as a result of steric considerations during the electrocyclic transformation of a dihalocyclopropane to a chiral allylic carbenium ion. These assignments were corroborated by the observation of net suprafacial addition of LTA to 1,2-cyclononadiene and an antarafacial mode of electrophilic addition in both the oxymercuration and oxythallation reaction.

(21) (a) Partch, R.; Monthony, J. *Tetrahedron Lett.* **1967**, 4427. (b) Heusler, K.; Loeliger, H. *Helv. Chim. Acta* **1969**, *52*, 1495.

(22) (a) Criegee, R. *Angew. Chem.* **1958**, *70*, 173. (b) Kabbee, H. J. *Justus Liebigs Ann. Chem.* **1962**, *656*, 204. Pande, K. C.; Winstein, S. *Tetrahedron Lett.* **1964**, 3393.

(23) (a) Bach, R. D.; Brummel, R. N.; Richter, R. F. *Tetrahedron Lett.* **1971**, 2879. (b) Bach, R. D.; Brummel, R. N. *J. Am. Chem. Soc.* **1975**, *97*, 453.

(24) Pirkle, W. H.; Boeder, C. W. *J. Org. Chem.* **1977**, *42*, 3697.

Experimental Section

General. Nuclear magnetic resonance spectral measurements were recorded on a Varian Associates A-60A or T-60 instrument. Peak positions are reported in parts per million from tetramethylsilane, which was used an internal standard. Peak areas were determined either by a Hewlett-Packard 3373B electronic integrator or by triangulation. Optical rotations were measured with a Perkin-Elmer Model 141 polarimeter. Elemental analyses were carried out by Midwest Microlab.

Thallic nitrate, thallic acetate, (+)-α-pinene, 1-octene, and triethylbenzylammonium chloride (TEBA) were obtained from the Aldrich Chemical Co. and were utilized without further purification. Lead tetraacetate was purchased from Arapahoe Chemicals and was freshly recrystallized from glacial acetic acid. *cis*-Cyclooctene was obtained from Columbian Carbon Co. Triglyme was dried by distillation from lithium aluminum hydride. Mercuric acetate, mercuric nitrate, mercuric oxide, methanol, and ethanol were obtained from the Mallinckrodt Chemical Works. Metallic lithium ribbon, methyl iodide, and methyllithium in ether were obtained from Matheson Coleman and Bell.

Partial Resolution of 1,2-Cyclononadiene (5). By the method of Caserio,[24] 3.5 g (0.025 mol) of boron trifluoride etherate was added to a solution of 1.02 g (0.027 mol) of sodium borohydride and 6.7 g (0.049 mol) of (+)-α-pinene, $[\alpha]^{25}_D$ +47° (neat), in 14 mL of triglyme. After 20 h of stirring at 0 °C, the reaction was cooled to −12 °C and 6.0 g (0.049 mol) of racemic 1,2-cyclononadiene was rapidly added. After 2.5 h, the unreacted 1,2-cyclononadiene was recovered by distillation; bp 25–60 °C (0.25 mm). A trace amount of α-pinene was subsequently removed by column chromatography on a 20% silver nitrate–alumina column. The 1,2-cyclononadiene had $[\alpha]^{25}_D$ −22.9° (*c* 2.1, CCl_4).

Reactions of 1,2-Cyclononadiene with Thallic Acetate in Methanol. (a). To a stirred solution of 0.061 g (0.50 mmol) of 1,2-cyclononadiene, $[\alpha]^{25}_D$ −15.6° (*c* 1.5, CCl_4), in 2 mL of methanol were added 0.204 g (0.50 mmol) of thallic acetate and 40 μL of boron trifluoride etherate. After 20 h of stirring at room temperature, the reaction was quenched by the addition of 1 mL of 3 M sodium hydroxide and 4 mL of 0.5 M sodium borohydride. After the aqueous solution was extracted with 10 mL of methylene chloride, the organic solution was washed with 3 × 5 mL of water. The volatiles were removed by rotary evaporation, and the crude allyl ether was chromatographed on a 2 ft × $^1/_2$ in. column of acid-washed alumina, with methylene chloride as the eluent. Evaporation of the solvent afforded 0.041 g (53.3%) of crude *cis*-3-methoxycyclononene that was homogeneous by gas chromatographic analysis. Preparative gas chromatography afforded **9a**, $[\alpha]^{25}_D$ +1.94° (*c* 2.2, CCl_4). A duplicate experiment afforded a sample having $[\alpha]^{25}_D$ +1.84° (*c* 1.8, CCl_4): IR (neat) 3030, 2950, 1450, 1100, 735 cm^{-1}; NMR (CCl_4) δ 0.9–2.3 (m, 12 H), 3.15 (s, 3 H), 4.0 (m, 1 H), 5.4 (m, 2 H). The product had infrared and NMR spectra that were identical with those of an authentic sample of *cis*-3-methoxycyclononene prepared by the methoxymercuration of 1,2-cyclononadiene.[5]

(b). To a stirred solution of 0.244 g (2 mmol) of 1,2-cyclononadiene, $[\alpha]^{25}_D$ −9.12° (*c* 6.74, CCl_4), in 4 mL of methanol were added 0.817 g (2 mmol) of thallic acetate and 40 μL of boron trifluoride etherate. After 72 h, the *cis*-3-methoxycyclononene isolated had $[\alpha]^{25}_D$ +1.38° (*c* 4.2, CCl_4).

Reaction of 1,2-Cyclononadiene with Thallic Acetate in Ethanol. To a stirred solution of 0.122 g (1 mmol) of 1,2-cyclononadiene, $[\alpha]^{25}_D$ −15.6° (*c* 1.5, CCl_4), in 4 mL of ethanol were added 0.408 g (1 mmol) of thallic acetate and 40 μL of boron trifluoride etherate. After 20 h of stirring at room temperature, 0.075 g (48%) of crude *cis*-3-ethoxycyclononene was isolated by preparative gas chromatography (6 ft × $^1/_4$ in., 10% SE-30 on Chrom W) and had $[\alpha]^{25}_D$ +2.96° (*c* 1.8, CCl_4). A duplicate experiment afforded a sample having $[\alpha]^{25}_D$ +2.78° (*c* 2.2, CCl_4): IR (neat) 3030, 2920, 2875, 1450, 1100, 740 cm^{-1}; NMR (CCl_4) δ 1.15 (t, 3 H), 1.5 (m, 12 H), 3.35 (m, 2 H), 4.18 (m, 1 H), 5.48 (m, 2 H). This product had IR and NMR spectra identical with those of an authentic sample of *cis*-3-ethoxycyclononene prepared by the ethoxymercuration of 1,2-cyclononadiene.[5]

Reactions of 1,2-Cyclononadiene with Thallic Acetate in Glacial Acetic Acid. (a). To a stirred solution of 0.061 g (0.5 mmol) of 1,2-cyclononadiene, $[\alpha]^{25}_D$ −15.6° (*c* 1.5, CCl_4), in 2 mL of glacial acetic acid were added 0.204 g (0.5 mmol) of thallic acetate and 40 μL of boron trifluoride etherate. After 20 h of stirring at room temperature, 5 mL of methylene chloride was added and the organic solution was washed with 3 × 5 mL of water. The volatiles were removed, affording a thallium adduct as a white solid. The solid was immediately suspended in 5 mL of dimethoxyethane and treated with 6 mL of 0.5 M $NaBH_4$. The reaction mixture was extracted with 3 × 5 mL of methylene chloride. The volatiles were removed, and the crude *cis*-3-acetoxycyclononene was chromatographed on a 1 ft × $^1/_2$ in. column of acid-washed alumina, with methylene chloride as the eluent. After the solvent was removed, the *cis*-3-acetoxycyclononene was collected by gas chromatography (6 ft × $^1/_4$ in., 10% SE-30 on Chrom W) and had $[\alpha]^{25}_D$ +0.6° (*c* 2.50, CCl_4). A duplicate experiment yielded *cis*-3-acetoxycyclononene having $[\alpha]^{25}_D$ +0.6° (*c* 2.47, CCl_4): IR (neat) 3080, 2950, 1738, 1450, 1250, 1020, 739 cm^{-1}; NMR (CCl_4) δ 1.1–1.8 (m, 12 H), 1.95 (s, 3 H), 2.0–2.3 (m, 1 H), 5.6 (m, 2 H). The product had IR and NMR spectra identical with those from an authentic sample of *cis*-3-acetoxycyclononene prepared by the acetoxymercuration of 1,2-cyclononadiene.

(b). To a stirred solution of 0.122 g (1 mmol) of 1,2-cyclononadiene, $[\alpha]^{25}_D$ −19.64° (*c* 6.74, CCl_4), in 4 mL of galcial acetic acid were added 0.408 g (1 mmol) of thallic acetate and 40 μL of boron trifluoride etherate. After 72 h, the product was isolated and the allylic acetate **9c** had $[\alpha]^{25}_D$ +0.45° (*c* 3.8, CCl_4).

2-[(Diacetato)thallio]-3-acetoxycyclononene. To a stirred solution of 0.122 g (1 mmol) of 1,2-cyclononadiene in 4 mL of glacial acetic acid were added 0.408 g (1 mmol) of thallic acetate and 80 μL of boron trifluoride etherate. After the reaction mixture was allowed to stir at room temperature for approximately 24 h, it was diluted with 6 mL of methylene chloride, and the acetic acid was removed by washing with 3 × 5 mL of water. The volatiles were removed by rotary evaporation, affording a white solid, mp 149–165 °C dec. Recrystallization from 1:9 methylene chloride–pentane gave amorphous white crystals, mp 170–171.5 °C dec. This experiment was repeated with 1,2-cyclononadiene having $[\alpha]^{25}_D$ −22.7°; the thallium adduct had $[\alpha]^{25}_D$ −0.7° (*c* 7.534, CH_2Cl_2): IR (KBr pellet) 2950, 1725, 1580, 1400, 1250, 1020 cm^{-1}; NMR ($CDCl_3$) δ 1.4–1.8 (m, 12 H), 2.07 (s, 6 H), 2.15 (s, 3 H), 5.45 (m, 1 H); mass spectrum, *m/e* (relative intensity) 445 (3), 443 (1), 386 (2), 384 (1), 265 (7), 263 (3), 249 (4), 247 (1), 205 (100), 203 (41), 181 (14), 139 (20), 122 (20), 121 (20), 120 (14), 94 (16), 93 (38). Anal. Calcd for $C_{15}H_{23}O_6Tl$: C, 35.77; H, 4.60. Found: C, 35.75; H, 4.59.

2-[(Diacetato)thallio]-3-methoxycyclononene. To a stirred solution of 0.122 g (1 mmol) of 1,2-cyclononadiene in 4 mL of methanol was added 0.408 g (1 mmol) of thallic acetate. After 20 h of stirring at room temperature, the reaction mixture was diluted with 5 mL of methylene chloride, and the organic phase was washed with 2 × 10 mL of water. The volatiles were removed by rotary evaporation, affording 0.40 g (84.4%) of a white solid. Recrystallization from 9:1 pentane–methylene chloride afforded the thallium adduct: mp 150–154 °C dec; IR (KBr pellet) 2950, 1590, 1400, 1080, 670 cm^{-1}; NMR ($CDCl_3$) δ 1.9–1.3 (m, 7 H), 2.07 (s, 6 H), 3.4 (br d, 3 H), 4.95 (s, 1 H); mass spectrum, *m/e* (relative intensity) 357 (4), 355 (1), 265 (2), 263 (1), 249 (3), 247 (1), 205 (100), 203 (42), 122 (11), 121 (21), 97 (9), 95 (11), 94 (13), 93 (26), 91 (12), 81 (24), 80 (21), 79 (32), 71 (19), 67 (29), 60 (11), 55 (13), 45 (14). Anal. Calcd for $C_{14}H_{23}O_5Tl$: C, 35.35; H, 4.87. Found: C, 35.52; H, 5.09.

Reactions of 1,2-Cyclononadiene with Thallic Nitrate in Methanol. (a). To a stirred solution of 0.122 g (1 mmol) of 1,2-cyclononadiene, $[\alpha]^{25}_D$ −22.7° (*c* 2.6, CCl_4), in 4 mL of methanol was added 0.444 g (1 mmol) of thallic nitrate. After 12 h of stirring at room temperature, the reaction was quenched by the addition of 1 mL of 3 M sodium hydroxide and 8 mL of 0.5 M sodium borohydride. The product was recovered by extraction with 3 × 5 mL of methylene chloride. The volatiles were removed by rotary evaporation, and the crude allyl ether was chromatographed on a 1 ft × $^1/_2$ in. column of acid-washed alumina, with methylene chloride as the eluent. Concentration of the solution afforded *cis*-3-methoxycyclononene, which upon isolation by gas chromatography (6 ft × $^1/_4$ in., 10% SE-30 on Chrom W) had $[\alpha]^{25}_D$ +1.18° (*c* 1.1, CCl_4). A duplicate experiment afforded **9a** having $[\alpha]^{25}_D$ +1.16° (*c* 0.95, CCl_4). The IR and NMR spectra were identical with those of an authentic sample of *cis*-3-methoxycyclononene.

(b). When the reaction was quenched after 3 h, the 3-methoxycyclononene that was isolated had $[\alpha]^{25}_D$ +2.11° (*c* 3.5, CCl_4). A duplicate experiment afforded a sample having $[\alpha]^{25}_D$ +2.26° (*c* 3.0, CCl_4).

Reaction of 1,2-Cyclononadiene with Thallic Nitrate in Ethanol. (a). To a stirred solution of 0.122 g (1 mmol) of 1,2-cyclononadiene, $[\alpha]^{25}_D$ −22.7° (*c* 2.6, CCl_4), in 3 mL of ethanol was added 0.444 g (1 mmol) of thallic nitrate. After 20 h of stirring at room temperature, 0.038 g (22.5%) of *cis*-3-ethoxycyclononene was isolated and had $[\alpha]^{25}_D$ +1.12° (*c* 1.7, CCl_4). A duplicate experiment afforded a sample having $[\alpha]^{25}_D$ +1.16° (*c* 0.95, CCl_4). The product had IR and NMR spectra identical with those of an authentic sample of *cis*-3-ethoxycyclononene.[5]

(b). When the reaction was quenched after 3 h, the 3-ethoxycyclononene that was isolated had $[\alpha]^{25}_D$ +2.68° (*c* 2.2, CCl_4). A duplicate experiment afforded a sample having $[\alpha]^{25}_D$ +2.68° (*c* 2.8, CCl_4).

Stability of Optically Active 1,2-Cyclononadiene (5). (a). Stability to Acidic Reaction Conditions. A 0.75 M solution of nitric acid in absolute methanol was combined with 0.0504 g of 1,2-cyclononadiene, $[\alpha]^{25}_D$ +9.12° (*c* 6.74, CCl_4), in a 1-mL volumetric flask. The solution was transferred to a polarimeter tube and the rotation observed. After 3 h, the rotation of the 1,2-cyclononadiene remained unchanged.

(b). Stability to Gas Chromatographic Collection Conditions. A sample of 1,2-cyclononadiene having $[\alpha]^{25}_D$ −15.21° was isolated utilizing a 15 ft × $^1/_4$ in., 10% SE-30 column at 115 °C. The injection-port temperature was 230 °C and the detector temperature was 270 °C. The helium flow was kept at 60 mL/min. The allene isolated under these conditions had $[\alpha]^{25}_D$ −15.15° (*c* 3.3, CCl_4).

(c). **Stability under Thallic Nitrate Reaction Conditions.** To 0.244 g (2 mmol) of 1,2-cyclononadiene, $[\alpha]^{25}_D$ −15.21°, in 4 mL of methanol was added 0.444 g (1 mmol) of thallic nitrate. After 3 h of stirring at room temperature, 8 mL of 0.5 M sodium borohydride was added, and the 1,2-cyclononadiene was recovered. After preparative gas chromatography, the 1,2-cyclononadiene exhibited no detectable rotation.

(d). Stability under Thallic Acetate Reaction Conditions. To 0.122 g (1 mmol) of 1,2-cyclononadiene, $[\alpha]^{25}_D$ −19.44° (*c* 3.94, CCl_4), in 4 mL of methanol were added 0.204 g (0.5 mmol) of thallic acetate and 40 μL of boron trifluoride etherate. After 24 h of stirring at room temperature, the unreacted 1,2-cyclononadiene was recovered by the addition of 8 mL of 0.5 M sodium borohydride and subsequent extraction with methylene chloride. The solvent was removed by rotary evaporation. The crude allene isolated by preparative gas chromatography had $[\alpha]^{25}_D$ −20.7° (*c* 0.82, CCl_4).

Exchange Reaction between 1-[(Nitrato)mercurio]-2-methoxyoctane and 1,2-Cyclononadiene. To a stirred solution of 0.112 g (1 mmol) of 1-octene in 4 mL of methanol was added 0.325 g (1 mmol) of mercuric nitrate. The reaction was stirred at room temperature for 1 h, and then 0.244 g (2 mmol) of 1,2-cyclononadiene was added. After 24 h, the reaction was quenched with 0.5 M sodium borohydride and extracted with methylene chloride. The volatiles were removed, and analysis of the residual oil by gas chromatography revealed the liberation of 1-octene and the formation of *cis*-3-methoxycyclononene. No 2-methoxyoctane was detected.

Attempted Exchange Reaction between 2-[(Acetato)mercurio]-3-methoxycyclononene and 1-Octene. To 0.244 g (2 mmol) of 1,2-cyclononadiene in 2 mL of methanol was added 0.318 g (1 mmol) of mercuric acetate. After 3 h of stirring at room temperature, 0.112 g (1 mmol) of 1-octene was added, and the reaction mixture was allowed to stir for 16 h. The reaction was quenched and the products were isolated in the manner described above. Analysis of the residual oil by gas chromatography revealed that 1,2-cyclononadiene, *cis*-3-methoxycyclononene, and 1-octene were the only volatile compounds in the reaction mixture. No exchange had taken place as evidenced by the absence of 2-methoxyoctane.

Attempted Reaction of 2-[(Diacetato)thallio]-3-methoxycyclononene with 1,2-Cyclononadiene in Ethanol. To 0.122 g (1 mmol) of 1,2-cyclononadiene in 4 mL of methanol was added 0.408 g (1 mmol) of thallic acetate. After 3 h of stirring at room temperature, the reaction was diluted with 10 mL of methylene chloride and the methanol was removed by washing the organic solution with 2 × 10 mL of distilled water. The methylene chloride solution, containing the thallium adduct, was combined with 4 mL of ethanol and 0.122 g (1 mmol) of 1,2-cyclononadiene. The methylene chloride was carefully removed by rotary evaporation, and the resulting ethanolic solution was allowed to stir at room temperature. After 16 h, the reaction was quenched, and the products were isolated in the usual manner. Analysis of the residual liquid by gas chromatography revealed only unreacted 1,2-cyclononadiene and *cis*-3-methoxycyclononene. No *cis*-3-ethoxycyclononene was observed.

Isomerization of *trans*-Cyclooctene by 2-[(Dinitrato)thallio]-3-methoxycyclononene. To 0.15 g (1.36 mmol) of 1,2-cyclononadiene in 4 mL of methanol was added 0.444 g (1 mmol) of thallic nitrate. After 3 h of stirring at room temperature, 0.110 g (1 mmol) of *trans*-cyclooctene was added, and the reaction was stirred an additional 3 h. After the reaction was quenched by the addition of 1 mL of 3 M sodium hydroxide and 8 mL of 0.5 M sodium borohydride, the aqueous mixture was extracted with 3 × 5 mL of methylene chloride. The methylene chloride solution was washed with 5 mL of aqueous sodium chloride and dried ($MgSO_4$). The volatiles were removed by rotary evaporation and the residual oil, analyzed by gas chromatography (15 ft × $^1/_4$ in., 10% SE-30 on Chrom W at 110 °C), showed only unreacted 1,2-cyclononadiene, *cis*-3-methoxycyclononene, and cyclooctene. The latter peak was further analyzed by using a 6 ft × $^1/_4$ in. 25% NMPN column, and *trans*-cyclooctene was shown to be absent. The infrared spectrum of the collected alkene was identical with those of an authentic sample of *cis*-cyclooctene.

Attempted Alkoxy Exchange with Thallic Salts. (a). Thallic Acetate. To 0.238 g (0.5 mmol) of 2-[(diacetato)thallo]-3-methoxycyclononene, prepared in the usual manner, was added 2 mL of ethanol. After 24 h of stirring at room temperature, the reaction was quenched by the addition of 4 mL of 0.5 M sodium borohydride. The aqueous mixture was extracted with methylene chloride and the combined organic extracts were dried ($MgSO_4$). After the volatiles were removed by rotary evaporation, analysis by gas chromatography revealed that no alkoxy exchange had occurred, as evidenced by the absence of any *cis*-3-ethoxycyclononene in the reaction mixture.

A similar experiment using 0.95 g (1.5 mmol) of nitric acid as a catalyst afforded identical results.

(b). Thallic Nitrate. To 0.62 g (0.5 mmol) of 1,2-cyclononadiene in 2 mL of methanol was added 0.222 g (0.5 mmol) of thallic nitrate. After 3 h of stirring at room temperature, the reaction mixture was diluted with 10 mL of methylene chloride, and the methanol was removed by washing the organic solution with 3 × 5 mL of water. Ethanol (2 mL) was added, and the methylene chloride was carefully removed by rotary evaporation. Nitric acid (0.095 g, 1.5 mmol) was added to the ethanolic solution, and the reaction was allowed to stir at room temperature for an additional 24 h. The reaction was quenched by the addition of 1 mL of 3 M sodium hydroxide and 4 mL of 0.5 M sodium borohydride. Gas chromatographic analysis of the recovered product revealed that no alkoxy exchange had occurred, as evidenced by the absence of *cis*-3-ethoxycyclononene in the reaction mixture.

Oxyplumbation of (*S*)-(−)-1,2-Cyclononadiene (5). With the procedure previously reported,[7] 0.366 g (3 mmol) of 1,2-cyclononadiene, $[\alpha]^{25}_D$ −99.8°, was added to a mixture of 2.7 g (6 mmol) of lead tetraacetate in 20 mL of glacial acetic acid. After the reaction mixture was allowed to stir overnight at room temperature, it was quenched and 0.206 g (38%) of 3-acetoxycyclononyne was obtained. The acetate was purified by preparative gas chromatography and had $[\alpha]^{25}_D$ +50.25° (*c* 1.7, CH_2Cl_2). A duplicate experiment afforded 3-acetoxycyclononyne having $[\alpha]^{25}_D$ +49.2° (*c* 1.8, CH_2Cl_2): NMR (CCl_4) δ 2.0 (s, 3 H), 0.86–2.37 (m, 12 H), 5.23 (m, 1 H); IR (neat) 2920–3000, 2260 (w), 1734, 1230, 1014 cm^{-1}.

Optical Purity of 3-Acetoxycyclononyne (12). The NMR spectrum of 30 mg of 3-acetoxycyclononyne, $[\alpha]^{25}_D$ +50.25° (*c* 1.7, CH_2Cl_2), in 1 mL of carbon tetrachloride gave an NMR signal at δ 2.1 (s, CH_3CO). Eu-Opt was added to the same NMR solution giving acetate signals in the ratio 32.7:67.3 (34.6% optically pure). A duplicate experiment utilizing 3-acetoxycyclononyne, $[\alpha]^{25}_D$ +49.22°, gave NMR signals in the ratio 35:65 (30% optically pure).

3-Acetoxycyclononene (9c). By a modified procedure described by Brown,[25] 0.206 g (1.1 mmol) of 3-acetoxycyclononyne, $[\alpha]^{25}_D$ +50.25° (*c* 1.7, CH_2Cl_2), was hydrogenated in ethanol, with nickel boride as a catalyst. When the uptake of hydrogen ceased, the solution was filtered and concentrated to afford 0.055 g (27.5%) of 3-acetoxycyclononene having $[\alpha]^{25}_D$ −24.63° (*c* 0.6, CH_2Cl_2), $[\alpha]^{25}_D$ −24.67° (*c* 0.91, CCl_4). A duplicate experiment afforded 3-acetoxycyclononene having $[\alpha]^{25}_D$ −24.92° (*c* 0.598, CH_2Cl_2).

3-Hydroxycyclononene (13). To 0.054 g (1.4 mmol) of lithium aluminum hydride in 4 mL of ether was added 0.07 g (0.38 mmol) of the combined samples of 3-acetoxycyclononene, $[\alpha]^{25}_D$ −24.75 ± 0.15°. After 3 h of stirring at room temperature, the reaction was quenched by the addition of several drops of water. The resulting solution was dried ($MgSO_4$) and concentrated to afford 0.031 g (58.5%) of 3-hydroxycyclononene. The alcohol was purified by preparative gas chromatography and had $[\alpha]^{25}_D$ −15.49° (*c* 1.3, CH_2Cl_2).

Product Distribution for the Reaction of 9,9-Dibromo-*trans*-bicyclo[6.1.0]nonane (7) with $AgClO_4$ in MeOH, EtOH, and HOAc. To a stirring solution of 1.6 g (7.8 mmol) of $AgClO_4$ in 6 mL of MeOH was added 0.30 g (1.1 mmol) of **7** with GLC internal standard cyclodecane. After 5 h, the reaction was quenched by the addition of excess KCl. The yield of 2-bromo-3-methoxycyclononene, by analytical GLC (155 °C, 12 ft, 10% SE-30) of the methanolic solution, was 78%. Subsequent GLC (105 °C, 3 ft, 25% NMPN) analysis of a preparative GLC-collected sample of the products established a mixture (92:8) of the cis and trans stereoisomers as determined by comparison with authentic samples.[7,18] A repeat of this experiment gave an overall yield of 93% and a cis:trans ratio of 91:9.

By the above procedure with ethanol solvent, the ethyl ether was obtained (97%) with a *cis*- to *trans*-2-bromo-3-ethoxycyclononene ratio of 95:5. A repeat of this study gave the same allylic ethyl ether (88%) with a cis–trans ratio of 96:4.

The above procedure was modified to employ a 1-h reaction time in HOAc solvent. Analysis by GLC (130 °C, 6 ft, 10% SE-30) established that the acetolysis product, 2-bromo-3-acetoxy-*cis*-cyclononene (**10c**), was obtained (80%) stereospecifically. A repeat of this experiment gave only the cis isomer (75%).

Optical Purity of the $AgClO_4$-Catalyzed Solvolysis Products of (−)-7. Solvolysis of Optically Pure 7 in Methanol. To a stirring solution of 0.71 g (3.4 mmol) of $AgClO_4$ in 2.5 mL of dry MeOH was added 0.14 g (0.5 mmol) of **7**, $[\alpha]^{25}_D$ −43.7° (*c* 3.0, CH_2Cl_2). After 10 min, the reaction was quenched by addition of chloride ion; preparative GLC (150 °C, 6 ft, 10% SE-30) afforded 2-bromo-3-methoxy-*cis*-cyclononene (**10a**):

(25) Brown, C. A.; Brown, H. C. *J. Am. Chem. Soc.* **1963**, *85*, 1003.

$[\alpha]^{25}_D$ +44.5° (*c* 2.64, CH_2Cl_2). An average of theee such experiments gave **10a** with $[\alpha]^{25}_D$ +43.2°.

The above procedure with a 20-min reaction time afforded **10a** with $[\alpha]^{25}_D$ +41.5° (*c* 5.85, CH_2Cl_2). A duplicate experiment gave **10a** with $[\alpha]^{25}_D$ +41.0° (*c* 2.62, CH_2Cl_2).

In **Ethanol.** To a stirring solution of 0.74 g (3.6 mmol) of $AgClO_4$ in 2.5 mL of dry EtOH was added 0.14 g (0.5 mmol) of **7**, $[\alpha]^{25}_D$ -43.7° (*c* 3.0, CH_2Cl_2). After 4 h at 25 °C, the reaction was quenched; preparative GLC (155 °C, 6 ft, 10% SE-30) afforded 0.06 g (0.25 mmol) of 2-bromo-3-ethoxy-*cis*-cyclononene (**10b**): $[\alpha]^{25}_D$ +36.0° (*c* 6.2, CH_2Cl_2). An average of three such experiments gave **10b** with $[\alpha]^{25}_D$ +35.9°. The above experiment with an 8-h reaction time gave **10b** with $[\alpha]^{25}_D$ +30.4° (*c* 3.03, CH_2Cl_2). An average of three such reactions gave $[\alpha]^{25}_D$ +30.3° for **10b**.

In **HOAc.** To a stirring solution of 0.44 g (2.2 mmol) of $AgClO_4$ in 3 mL of HOAc was added 0.17 g (0.6 mmol) of **7**, $[\alpha]^{25}_D$ +45.2° (*c* 3.24, CH_2Cl_2). After 30 min, the reaction was quenched; preparative GLC (140 °C, 6 ft, 10% SE-30) afforded 0.05 g (0.19 mmol) of 2-bromo-3-acetoxy-*cis*-cyclononene (**10c**): $[\alpha]^{25}_D$ -6.7° (*c* 4.93, CH_2Cl_2). An average of three such experiments gave **10c** with $[\alpha]^{25}_D$ -7.1°.

The reaction of **7**, $[\alpha]^{25}_D$ -43.7° (*c* 3.0, CH_2Cl_2), under the above conditions for 1 h afforded **10c** with $[\alpha]^{25}_D$ +7.7° (*c* 4.8, CH_2Cl_2). A repeat of this experiment gave **10c** with $[\alpha]^{25}_D$ +7.5° (*c* 5.8, CH_2Cl_2).

Reduction of 2-Bromo-3-methoxy-*cis*-cyclononene (10a). In a typical experiment, 0.06 g (0.26 mmol) of **10a**, $[\alpha]^{25}_D$ +41.5° (*c* 5.85, CH_2Cl_2), was added to a solution of 0.03 g (1.3 mmol) of sodium metal in 3 mL of NH_3(l). After 1 h, the reaction was quenched by the addition of NH_4Cl; preparative GLC (150 °C, 6 ft, 10% SE-30) afforded 3-methoxy-*cis*-cyclononene (**9a**); $[\alpha]^{25}_D$ -12.9° (*c* 1.04, CH_2Cl_2). An average of four such reactions gave **9a** with $[\alpha]^{25}_D$ -13.0°.

Reduction of 2-Bromo-3-ethoxy-*cis*-cyclononene (10b). A Na/NH_3(l) reduction of **10b**, $[\alpha]^{25}_D$ +35.8° (*c* 6.2, CH_2Cl_2), as described above, gave, after preparative GLC (150 °C, 6 ft, 10% SE-30), 3-ethoxy-*cis*-cyclononene (**9b**); $[\alpha]^{25}_D$ -20.6° (*c* 2.2, CH_2Cl_2). A repeat of this experiment gave **9b** with $[\alpha]^{25}_D$ -20.0° (*c* 2.1, $CHCl_2$).

Reduction of 2-Bromo-3-acetoxy-*cis*-cyclononene (10c). To a slurry of 0.015 g (0.4 mmol) of $LiAlH_4$ in 5 mL of dry Et_2O was added 0.035 g (0.2 mmol) of **10c**, $[\alpha]^{25}_D$ +7.5° (*c* 5.8, CH_2Cl_2). After 1 h, the reaction was quenched by titration with 0.025 mL of H_2O; preparative GLC (130 °C, 6 ft, 10% SE-30) afforded 2-bromo-*cis*-cyclononen-3-ol; $[\alpha]^{25}_D$ +9.3° (*c* 2.2, CH_2Cl_2).

Enantiomeric Purity of 2-Bromo-3-acetoxy-*cis*-cyclononene (10c). A routine NMR of an aliquot, 0.25 mL, of a solution of 0.153 g (5.9 mmol) of **10c** ($[\alpha]^{25}_D$ -11.1° (*c* 15.3 CCl_4); $[\alpha]^{25}_D$ -8.5 (*c* 3.85 CH_2Cl_2)) in 1 mL of CCl_4 gave an NMR signal at δ 2.02 (s, CH_3CO). A 0.07-g (0.1 mmol) sample of Eu-Opt ($Eu(C_{12}H_{14}F_3O_2)_3$) was added to the same NMR solution, giving acetate signals at δ 3.86 (s) and 3.98 (s). An average of 26 integrations of the relative areas of these NMR signals gave an upfield:downfield ratio of 37.5:62.5 (25% optically pure). A repeat of this NMR study gave, after 36 integrations, an upfield:downfield peak ratio of 38.9:61.1 (22.2% optically pure).

In a control experiment, racemic **10c**, using the above procedure, afforded acetate signals in the ratio of 50.3:49.7 (upfield:downfield).

Conversion of 10c to 2-Bromo-3-methoxy-*cis*-cyclononene (10a). To a slurry of 0.04 g (1 mmol) of 95% $LiAlH_4$ in 3 mL of dry Et_2O was added 0.1 g (0.4 mmol) of **10c**, $[\alpha]^{25}_D$ -8.8° (*c* 5.8, CH_2Cl_2). After 1 h, the reaction was quenched by titration with H_2O; the ether phase was decanted and charged with 0.25 g (5.9 mmol) of a 57% NaH oil dispersion. To this mixture was added 0.7 g (4.9 mmol) of MeI. After 3 h, the reaction was quenched by the addition of H_2O; preparative GLC (140 °C, 6 ft, 10% SE-30) afforded **10a**: $[\alpha]^{25}_D$ -24.0° (*c* 2.80, CH_2Cl_2). A repeat of this experiment gave **10a**; $[\alpha]^{25}_D$ -23.9° (*c* 3.27, CH_2Cl_2).

Conversion of 10c to 2-Bromo-3-ethoxy-*cis*-cyclononene (10b). The ethereal solution from the $LiAlH_4$ reduction of 0.2 g (0.8 mmol) of **10c**, $[\alpha]^{25}_D$ -8.8° (*c* 5.8, CH_2Cl_2), as described above was concentrated and the residue taken up in 10 mL of dry THF. This solution was treated with 1 g (24 mmol) of a 57% dispersion of NaH in oil and 2 g (13 mmol) of EtI. After 36 h, the reaction was quenched by the addition of H_2O; preparative GLC (140 °C, 6 ft, 10% SE-30) gave **10b**: $[\alpha]^{25}_D$ -21.6° (*c* 4.95, CH_2Cl_2). Collection of a second aliquot from this reaction gave **10b**: $[\alpha]^{25}_D$ -21.9°° (*c* 4.21, CH_2Cl_2).

Acknowledgment. We gratefully acknowledge support fr .. the National Institutes of Health (Grant No. ES-00761-09) and the National Science Foundation (Grant No. CHE-80-06520).

Registry No. (*S*)-**5**, 18526-52-8; (±)-**5**, 24373-47-5; (*S*)-**9a**, 54193-03-2; (*R*)-**9a**, 35018-79-2; (*R*)-**9b**, 35018-81-6; (*S*)-**9b**, 81626-10-0; (*R*)-**9c**, 35018-85-0; (*S*)-**9c**, 35018-87-2; (*S*)-**10a**, 54165-74-1; (*R*)-**10a**, 35018-78-1; (*R*)-**10b**, 35018-80-5; (*S*)-**10b**, 81655-22-3; (*R*)-**10c**, 35018-82-7; (*S*)-**10c**, 81626-11-1; (*R*)-**11a**, 31001-84-0; (*R*)-**11b**, 81655-23-4; (*R*)-**11c**, 81626-12-2; (*R*)-**12**, 35018-84-9; (*R*)-**13**, 81655-24-5; (*S*)-**17**, 54156-78-4; (*S*)-**18**, 54156-79-5; **19**, 81626-13-3; (*S*)-[(acetato)mercurio]-3-methoxy-*cis*-cyclononene, 81626-14-4; *trans*-cyclooctene, 931-89-5; *cis*-cyclooctene, 931-87-3; (*R*)-2-bromo-*cis*-cyclononen-3-ol, 81655-25-6; (1*R*,8*R*)-**7**, 26216-41-1; (1*S*,8*S*)-**7**, 26216-40-0.

Unusual Solvent Effects in the Wittig Reaction of Some Ketones Indicating Initial One-Electron Transfer

George A. Olah* and V. V. Krishnamurthy

Contribution from the Hydrocarbon Research Institute and Department of Chemistry, University of Southern California, Los Angeles, California 90007. *Received October 16, 1981*

Abstract: Investigation of the Wittig reaction of adamantanone, 1, and some other ketones in various solvent systems with alkylidenetriphenylphosphoranes indicates an initial one-electron transfer from the ylide to the carbonyl group. In hydrogen-donor solvents, the hydrogen abstraction from the solvents by the radical ions generated by the one-electron transfer competes considerably with the olefin-forming Wittig reaction, giving unexpected reduction of the carbonyl group. It is shown that such reductions become the major pathway when steric hindrance affects the usual olefin-forming Wittig reaction.

The Wittig reaction is one of the most widely used reactions in synthetic organic chemistry. There are many reviews on the synthetic and mechanistic aspects of this reaction.[1] The widely accepted mechanism for the formation of olefins from ketones and alkylidenetriphenylphosphoranes is outlined in Scheme I.[2] The intermediacy of the betaine, A, has been proven earlier.[3]

We now wish to report a previously unrecognized solvent effect, which is reflected in the products formed in the Wittig reaction. On the basis of this study we propose an initial one-electron transfer from the alkylidenetriphenylphosphorane to the carbonyl

(1) For example, see: (a) Maercker, A. *Org. React. (N.Y.)* **1965**, *14*, 270. (b) Trippett, S. *Q. Rev., Chem. Soc.* **1963**, *17*, 406. (c) Boutagy, J.; Thomas, R. *Chem. Rev.* **1974**, *74*, 87.

(2) See ref 1a and references therein.

(3) (a) Wittig, G.; Schollkopf, U. *Chem. Ber.* **1954**, *87*, 1318. (b) References in 1a.

0002-7863/82/1504-3987$01.25/0