edged. We would like to thank Drs. David L. Dalrymple and Roger Crecely for obtaining and helping to interpret the ^{13}C NMR data.

Registry No.—**9h,** 63569-86-8; **9i,** 63569-87-9; **9j,** 63569-88-0; **9k,** 63569-89-1; **9r,** 63569-90-4; **9s,** 63569-91-5; **9t,** 63569-92-6; **9u,** 63569-93-7; **9v,** 53569-94-8; **9x,** 63569-95-9; **11t,** 63569-96-0; **11x,** 63569-97-1; **12c,** 63569-98-2; **12d,** 63569-99-3; **12e,** 63570-00-3; **12f,** 63570-01-4; **12g,** 63570-02-5; **12h,** 63570-03-6; **12i,** 63570-04-7; **12j,** 63570-05-8; **12k,** 63570-06-9; **12l,** 63570-07-0; **12m,** 63570-08-1; **12n,** 63570-09-2; **12o,** 63570-10-5; **12p,** 63570-11-6; **12q,** 63570-12-7; **12r,** 63570-13-8; **12s,** 63570-14-9; **12u,** 63570-15-0; **12v,** 63570-16-1; **12w,** 63570-17-2; **12x,** 63570-18-3; **13,** 22610-15-7; **14,** 2091-46-5; **17** charged form, 63570-19-4; **17** uncharged form, 63570-20-7; **18** charged form, 63570-21-8; **18** charged form, 63570-22-9; **22,** 5344-88-7; **23,** 63570-23-0; **24** charged form, 63570-24-1; **24** unchanged form, 63570-25-2; **25,** 33487-48-8; **26a,** 104-55-2; **26b,** 623-30-3; **26c,** 4170-30-3; **26d,** 101-39-3; **26e,** 122-57-6; **26f,** 623-15-4; **26g,** 94-41-7; **26h,** 4070-75-1; **26i,** 5443-49-2; **26j,** 1192-88-7; **26k,** 25090-33-9; **26l,** 13417-49-7; **26m,** 6140-65-4; **26n,** 5682-83-7; **26o,** 5679-13-0; benzaldehyde, 100-52-7; 4-chlorobenzaldehyde, 104-88-1.

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Estimation of Allene Optical Purities by Nuclear Magnetic Resonance

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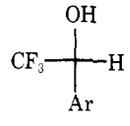
Methoxymercuration of chiral allenes affords chiral ethers, the enantiomeric purity and absolute configuration of which are related to those of the allenic precursor. Enantiomeric purity and absolute configuration of these allene derivatives can be determined by NMR using (*R*)-(−)-2,2,2-trifluoro-1-(9-anthryl)ethanol (**1a**) as a chiral solvating agent. A solvation model is advanced to account for the origin and sense of the observed NMR nonequivalence of the enantiomeric derivatives in the presence of **1a**.

Despite considerable interest in the chemistry of chiral allenes, there is no general experimental method for the determination of enantiomeric purity of allenes lacking additional functionality. However, Brewster has calculated the rotational values expected for several chiral allenes including those without additional functional groups.[1] Chemical transformation of a chiral allene to a known chiral reference compound can provide enantiomeric purity data, although this approach is seldom used since most reactions that might be employed to modify the allenic functionality do not proceed stereospecifically. Thus far, the use of chiral solvating agents (CSA) as a direct method for determining enantiomeric purities of chiral allenes has been unsuccessful unless an additional "handle" is present.[2] An alternate indirect approach in which the chiral allene is stereospecifically converted to a chiral compound, the enantiomeric purity of which is then determined by NMR using a CSA, is the subject of the present paper.

Prior work with chiral type **1** fluoro alcohols has shown that these CSA render nonequivalent the NMR spectra of enantiomeric benzylic, allylic, or propargylic alcohols and their ethers. The oxymercuration of allenes in H_2O or methanol, believed to be a highly stereospecific reaction, affords mercury-containing allylic alcohols or methyl ethers. Owing to the sharp singlets arising from methoxyl groups, methoxymercuration is well suited to the overall process for NMR determination of enantiomeric purity. We have methoxymercurated several partially resolved simple allenes and used a type



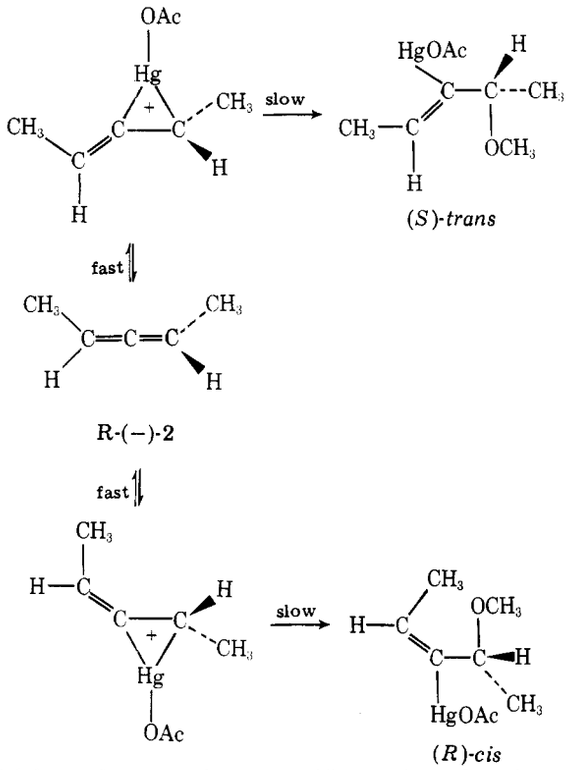
1

1 CSA to determine enantiomeric composition of the product ethers.

Methoxymercuration of allenes with mercuric acetate in methanol usually affords both cis and trans adducts and is considered to occur by the mechanistic pathway shown in Scheme I.[3] This scheme predicts that the two adducts will be of opposite chirality.[3]

Reaction of (*R*)-(−)-2,3-pentadiene (**2**), $[\alpha]^{25}_D$ −14.5° (1, Et_2O), with $Hg(OAc)_2$ in dry methanol at 25 °C followed by exchange of acetate for chloride affords a 6:1 ratio of trans:cis 3-chloromercuri-4-methoxy-2-pentenes, **3t** and **3c**, respectively. In CCl_4 solution with 3 equiv of (*R*)-(−)-2,2,2-trifluoro-1-(9-anthryl)ethanol (**1a**) the mixture of **3t** and **3c** shows NMR nonequivalence of the enantiotopic methoxyl resonances for each isomer. Although the sense of nonequivalence and enantiomeric purity of **3c** in the mixture could not be reliably determined due to the proximity of other signals, the enantiomeric purity of (*S*)-**3t**, the major isomer, was ascertained to be 9.2%, with the methoxyl signal of the major enantiomer occurring at a higher field than that of the minor enantiomer (high field "sense" of nonequivalence). This value represents the *minimum* enantiomeric enrichment for **2**,

Scheme I



which hence has a *maximum* specific rotation value of −158°. After separation of **3c** and **3t** by preparative GLPC (4 ft × 0.25 in., 20% SE-30 on Chromosorb W, 115 °C), **3c** showed a low-field sense of methoxyl nonequivalence and 6% enantiomeric excess.

Although too little of the cis isomer was obtained to establish its configurational stability during GLPC, the major trans isomer **3t** does undergo partial racemization during gas chromatography. The observation of opposite senses of methoxyl nonequivalence for **3c** and **3t** strongly suggests that these isomers are formed with opposite absolute configurations. This point will be elaborated further during the discussion of the mode of solvation of allyl ethers by CSA **1a**.

Methoxymercuration of (*S*)-(+)-3,4-heptadiene (**4**), $[\alpha]^{25}_{D}$ +33.8° (2 $CHCl_3$), at −78 °C affords a 19:1 mixture of the trans and cis chloromercurals **5t** and **5c**. Again using CSA **1a**, **5t** was found to be 33% enantiomerically enriched. Reduction of the amount of **5c** present through use of low-reaction temperatures simplifies the NMR analysis of enantiomeric purity. The results of similar experiments on other allenes are reported in Table I. In each instance, enantiomeric purity and absolute configuration of the chloromercurals could be established by NMR, thus also establishing the absolute configuration and minimum enantiomeric purity of the initial allene.

The accuracy of these determinations of enantiomeric purities of chiral allenes is dependent on the stereospecificity of the methoxymerucration reaction. Different allenes might well undergo methoxymercuration with different degrees of stereospecificity. Presently, it is our view that simple acyclic allenes, such as those in Table I, undergo methoxymercuration at −78 °C with high and perhaps complete stereospecificity. Cyclic allenes may show lessened stereospecificity. For example, Bach[4] has suggested that, for 1,2-cyclononadiene, the stereospecificity of ethoxymercuration is a function of the mercurating agent. In Bach's hands, mercuric acetate, the most commonly used reagent for oxymercuration, led, after demercuration, to allyl ether **7** that had but 81% of the rotatory power of the same adduct obtained directly from **6** using ethylmercuric acetate and boron trifluoride (Scheme II).[5]

Scheme II

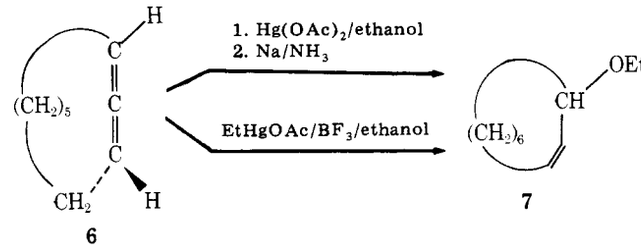
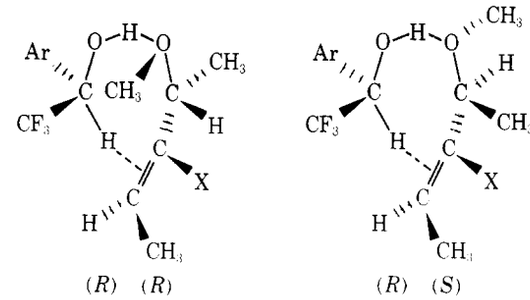


Chart I



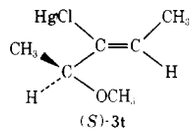
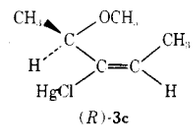
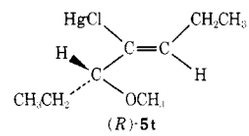
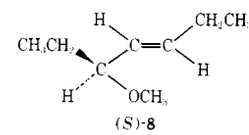
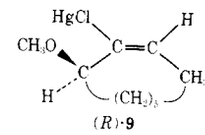
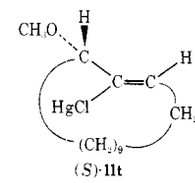
X = HgCl or H

However, methoxymercuration of partially resolved (*R*)-**4**, $[\alpha]^{25}_{D}$ −26.4°, using ethylmercuric acetate/BF_3 at 0 °C leads to *trans*-**8** of an enantiomeric purity (25%) such that the maximum absolute rotation calculated for allene **4** by this method is not significantly different from that calculated by the alternate methoxymercuration procedure (Table I). Thus, the two methoxymercuration reactions proceed with the same degree of stereospecificity. Note also (Table I) that methoxymercuration of **2** proceeds with the same stereospecificity at 25 °C as it does at −78 °C. These results are consistent with (but do not require) essentially complete stereospecificity during methoxymercuration of acyclic allenes.

Solvation Model. The NMR nonequivalence shown by the enantiomers of a variety of solute types in the presence of chiral fluoro alcohols such as **1a** appears to fit a uniform model.[7] Chart I shows the application of this type of solvation model to the allyl ethers arising from methoxymercuration of allenes. The carbinol hydrogen bonds to a primary basic site, the methoxyl oxygen, and a weaker secondary interaction between the carbinyl hydrogen and the second basic site, the π electrons in the double bond, serves to populate chelate-like conformations of the two diastereomeric solvates. The diastereomeric solvates show NMR nonequivalence due to the stereochemically dependant shielding exerted by the aryl substituent of the carbinol. For steric reasons, a significantly populated rotomer in these solvates is one in which the methoxyl group is approximately eclipsed with the carbinyl hydrogen of the ether, the smaller of the three remaining substituents upon the chiral center. In this rotomer, the anthryl substituent of **1a** causes the methoxyl signal of (*S*)-**3t** to occur at a higher field than does the methoxyl signal of (*R*)-**3t**. The model takes no cognizance of whether the ether has cis or trans geometry about the double bond or whether or not it contains mercury. Neither structural variation appears to perturb the correlation between sense of nonequivalence and absolute configuration.

Summary. Reaction of chiral allenes with mercuric acetate–methanol or with ethylmercuric acetate–BF_3–methanol leads to chiral methyl allyl ethers, the enantiomeric purity and absolute configuration of which can be determined by NMR using a chiral solvating agent. This approach is most easily applied to allenes having identical substituents on the termini of the allenic group. Dissimilarly substituted allenes may af-

Table I. Methoxymercuration of Optically Enriched Chiral Allenes

Allene, $[\alpha]^{25}D$	Registry no.	Product	Registry no.	ee[b] / yield[a]	Max absolute rotation[c]	Sense of nonequivalence in 1a[e,f]
(*R*)-(−)-2,3-Pentadiene (2), −14.5° (1, Et_2O)	20431-56-5	 (*S*)-3t	63597-50-2	9.2% / (86%)	(−)158°	H[g] (1.6)[h]
		 (*R*)-3c	63597-51-3	– / (14%)		L (1.5)
(*R*)-(−)-2, −29.6° (2.6, Et_2O)		(*S*)-3t		19.0% / (95%)[d]	(−)156°	H (1.6)
(*S*)-(+)-3,4-Heptadiene (4), +33.8° (2, $CHCl_3$)	20431-62-3	 (*R*)-5t	63534-25-8	33.1% / (94%)[d]	(+)102°	L (1.6)
(*R*)-(−)-4, −22.7° (2.5, $CHCl_3$)	34862-66-3	(*S*)-5t	63534-26-9	21.6% / (96%)[d]	(−)105°	H (1.6)
(*R*)-(−)-4, −26.4° (1, $CHCl_3$		 (*S*)-8	63534-27-0	25.0% / (>90%)	(−)106°	H[g] (1.7)
(*R*)-(+)-1,2-Cyclononadiene (6), +18.8° (2.8, $CHCl_3$)	26114-92-1	 (*R*)-9	63597-52-4	8.4% / (100%)	(+)223°	L[g] (1.8)
(*R*)-(+)-1,2-Cyclotridecadiene (10), +15.2° (3.4, $CHCl_3$)	18526-51-7	 (*S*)-11t	63597-53-5	7.8% / (86%)	(+)195°	H (1.8)

[a] Number in parenthesis is percent of product in product mixture. [b] Calculated from areas under methoxyl resonances in the presence of 1a. [c] Calculated from enantiomeric excess of mercural as *minimum* enantiomeric excess of allene. [d] Methoxymercurated at −78 °C. [e] A 3:1 1a:substrate ratio in CCl_4. [f] Nonequivalence of methoxyl resonances. [g] NMR data was obtained using (*S*)-(+)-2,2,2-trifluoro-1-(9-anthryl)ethanol. Senses of nonequivalence have been inverted here for uniformity and clarity. [h] Magnitude of nonequivalence in Hz at 100 MHz. H and L refer to high- or low-field sense of nonequivalence.

ford regioisomers, and the additional resonances may complicate spectral interpretation. Liquid chromatographic separation of the regioisomers would obviate this difficulty.

Experimental Section

Mercuric acetate methoxymerucration products (except **5t**) were characterized from previously reported data. Carbinol **1a** was prepared as previously reported.[7] Optically enriched allenes were prepared by asymmetric hydroboration[8] or by a modification of Crabbé's method[9] that will be reported elsewhere.

Methoxymercuration of Allenes with $Hg(OAc)_2$ in Methanol. Methoxymercuration was carried out at 25 °C according to the method of Caserio.[3] The following procedure is typical for methoxymercurations at −78 °C. To a stirred solution of $Hg(OAc)_2$ (66 mg, 0.21 mmol) in dry methanol (15 mL) cooled in a dry ice/isopropyl alcohol bath was added 4 (20 mg, 0.21 mmol) in 1 mL of diethyl ether. The reaction was stirred at −78 °C for 9 h after which Na_2CO_3 (28 mg, 0.26 mmol) was added. The reaction mixture was warmed to room temperature, methanol was removed under reduced pressure, and an aqueous solution of NaCl (12 mg, 0.21 mmol) was added to the remaining oil. Extraction of the chloromercural into $CHCl_3$ (four 5-mL portions), drying of the organic layer ($MgSO_4$), filtration, and evaporation of the $CHCl_3$ afforded a colorless oil, **5t** and **5c** (19:1 by NMR): NMR (**5t**) (CCl_4) δ 0.8 (t, 3, J = 7 Hz, $CHOCH_3CH_2\mathbf{CH_3}$), 1.05 (t, 3, J = 7 Hz, $C{=}CHCH_2\mathbf{CH_3}$) 1.2–1.7 (m, 2, $CHOCH_3$–$\mathbf{CH_2}$–CH_3), 2.2 (quintet, 2, $C{=}CH\mathbf{CH_2}CH_3$), 3.2 (s, 3, $\mathbf{OCH_3}$), 3.5 (t, 1, J = 6 Hz, $\mathbf{CH}OCH_3$), 6.15 (t, 1, J = 8 Hz, C=C**H**).

Methoxymercuration of (*R*)-(−)-3,4-Heptadiene with $EtHgOAc/BF_3{\cdot}Et_2O$ in Methanol. The procedure described by Bach[4] was followed using (*R*)-(−)-**4**, $[\alpha]^{25}D$ −22.6° (1, $CHCl_3$) and methanol except that the reaction was conducted for 24 h at 0 °C. Control experiments using 5,6-undecadiene and GLPC analysis showed that this reaction proceeds at a negligable rate at −78 or −30 °C. Allylic ether **8** (>90% trans)[10] was isolated by preparative GLPC (4.5 ft × 0.25 in., SE-30 on Chromosorb W, 60°C): NMR (CCl_4) δ 0.85 (t, 3, J = 7 Hz, $CHOCH_3CH_2\mathbf{CH_3}$), 1.01 (t, 3, J = 7 Hz, $C{=}CHCH_2\mathbf{CH_3}$), 1.45 (m, 2, $CHOCH_3\mathbf{CH_2}CH_3$), 2.1 (quintet, 2, $C{=}CH\mathbf{CH_2}CH_3$), 3.15 (s, 3, $\mathbf{OCH_3}$) 3.3 (m, 1, $\mathbf{CH}OCH_3$), 5.0–5.7 (m, 2, **HC=CH**). Ether **8** was stable to racemization under GLPC conditions.

Acknowledgment. This work has been partially funded by grants from the National Science Foundation and the National Institutes of Health.

Registry No.—(*R*)-**5c**, 63534-28-1; $Hg(OAc)_2$, 1600-27-7.

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(5) If the difference in rotations of Bach's two samples of **7** reflects the difference in stereospecificities of the mercurations and not a partial racemization of the organo mercuric acetate upon demercuration to give **7**, then an adjustment can be made of the maximum rotation for 1,2-cyclononadiene, $[\alpha]^{25}_{max}$ = 223° × 0.81 = 181°. This rotation is in close agreement with Moore's calculated absolute rotation.[6]
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Dynamic Stereochemistry of Imines and Derivatives. 12. Bis(*N*-alkylimines) Derived from Tetramethylcyclobutane-1,3-dione[1]

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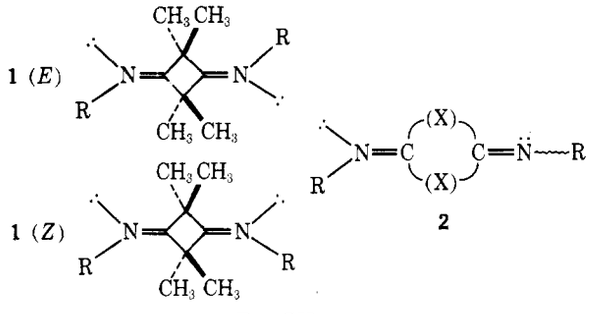
A series of bisimines **1** where R = CH_3, CH_2CH_3, $CH(CH_3)_2$, $C(CH_3)_3$, and C_6H_{11} has been prepared in high yield using $TiCl_4$ as catalyst. The *tert*-butyl compound exists exclusively in the *E* configuration, but the other less hindered compounds showed 20–30% *Z* isomer at equilibrium in solution. It is proposed that the *Z* isomer is destabilized by a buttressing interaction between the ring methyl groups and the flanking *N*-alkyl substituents, though dipolar interactions were also evaluated. The rates of *E*–*Z* isomerization were determined, where appropriate, by direct equilibration at 35 °C and by dynamic NMR spectroscopy at higher temperatures. The $\Delta G^{\ddagger}$ values lie in the range 24.8–21.8 kcal mol^{-1} and decrease with increasing bulk of the *N*-alkyl group. The mono(*tert*-butylimine) **4** shows a markedly lower $\Delta G^{\ddagger}$ value of 19.2 kcal mol^{-1}. Some $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ data were also determined, and the results are consistent with a lateral shift pathway for isomerization. ^1H and ^{13}C chemical shift data for both isomers are tablulated and discussed.

Tetramethylcyclobutane-1,3-dione should, in principle, condense with primary amines, RNH_2, to form bisimines of structure **1**. These compounds are capable of exhibiting an interesting type of *E*–*Z* isomerism, and are examples of the more general representation depicted in **2**. Other bisimines



a, R = CH_3
b, R = CH_2CH_3
c, R = $CH(CH_3)_2$
d, R = $C(CH_3)_3$
e, R = cyclohexyl

within the scope of this general structure are 1,4-diazabutatriene[3] (**2**, X = –) and the 1,4-benzoquinone bisimines (**2**, X = CH=CH).[4]

The ring methyl groups in **1** provide a useful handle for assigning the stereochemistry by NMR spectroscopy. Tetramethylcyclobutane-1,3-dione has been reported to form bisimines with aromatic amines in the presence of an acid catalyst, but alkylamines were found to give 2,2,4-trimethyl-3-oxopentanamides by ring cleavage.[5] Only in the case where R = cyclohexyl was the bis(*N*-alkylimine) **1** isolated in low yield (ca. 15%). Worman and Schmidt[6] have shown by ^1H NMR spectroscopy that these bisimines were formed as an *E*–*Z* isomeric mixture. The ring methyl signals from both isomers were reported to coalesce on raising the sample temperature above 100 °C, but no kinetic data were reported.

We now report the preparation of a series of *N*-alkyl compounds with structure **1** in good yield, including the very hindered compound where R = *tert*-butyl. The isomer distribution has been investigated and the rates of isomerization have been determined by direct thermal stereomutation and dynamic NMR spectroscopy.

Results and Discussion

Synthesis and Stereochemistry. Titanium(IV) chloride has proven to be a remarkably effective catalyst for the condensation of amines with a wide range of aldehydes and ketones, including relatively unreactive diaryl ketones.[7-9] This method also enabled the new bisimines **1a–d** to be prepared from tetramethylcyclobutane-1,3-dione in high yield. Prolonged reaction in boiling toluene was required, presumably due to steric hindrance around the carbonyl groups. The biscyclohexyl compound **1e**, which had been prepared previously in low yield,[5] was obtained in 65% yield by the above method.

^1H and ^{13}C NMR spectra showed that the bisimines **1a–c** (R = CH_3, CH_2CH_3, and $CH(CH_3)_2$) were present as an *E*/*Z* isomer mixture in solution. Stereochemical assignment was straightforward as the ring carbons C-2 and C-4 and their *gem*-dimethyl groups are nonequivalent in the *Z* form but isochronous in the *E* isomer (as noted previously for other compounds of this type[6]).

The position of equilibrium markedly favors the *E* configuration (Table I), hence the configuration at one nitrogen