Synthesis, Absolute Configuration, and Optical Purity of Chiral Allenes

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This review deals with the synthesis of chiral allenes, including those which occur in nature, together with the determination of their absolute configuration and optical purity. The treatment of these subjects is preceded by a summary of the nomenclature used in this article. The literature has been surveyed through December 1971.

1. Naturally Occurring Chiral Allenes
2. Asymmetric Synthesis of Chiral Allenes
3. Resolution by Formation of Diastereomers
4. Synthesis from a Chiral Precursor containing One or More Chiral Centers or Exhibiting Molecular Dissymmetry
5. Determination of Absolute Configuration
6. Determination of Optical Purity

Es wird eine Übersicht über die Synthese chiraler Allene gegeben, einschließlich der in der Natur vorkommenden. Die Bestimmung der absoluten Konfiguration und der optischen Reinheit wird in eigenen Abschnitten besprochen. Zu Anfang wird die in diesem Artikel verwendete Nomenklatur erklärt. Die Literatur ist bis Dezember 1971 berücksichtigt.

Several excellent reviews related to allene chemistry have appeared through the years, in which the synthesis, the physical and chemical properties of allene and its derivatives are summarized[1]. However, to date no comprehensive review on the stereochemistry of chiral allenes exists.

The purposes of this article are:

- to summarize the data pertaining to the subject of this review for the principal naturally occuring chiral allenes;
- to survey the methods used for the synthesis of chiral allenes, and the determination of their absolute configuration and optical purity.

Nomenclature

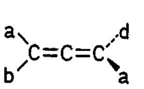
Allenes are defined as "asymmetric" when they contain no element of symmetry. This is, for example, the case when:

(a) the ends of the allenic group bear three or four different types of achiral substituents (e.g., **1** or **2**, respectively),

(b) one hydrogen atom of propadiene is substituted by a group containing one or more chiral centers (e.g. **3**);

(c) both hydrogen atoms of a methylene group of propadiene are substituted by two configurationally and structurally identical groups containing one or more chiral centers (e.g. **4**);

(d) two hydrogen atoms on different carbon atoms of propadiene are substituted by two structurally identical groups which are enantiomerically related to each other (e.g. **5**).



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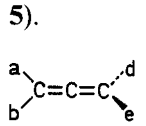

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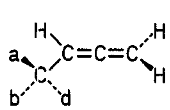

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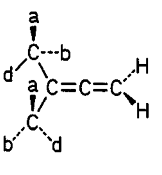

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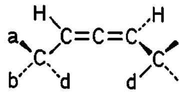

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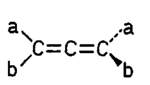
Allenes containing a C_2 proper axis of rotation are defined as "dissymmetric". This is, for example, the case when:

(a) both ends of the allenic group bear two different achiral groups (e.g. **6**);

(b) two hydrogen atoms on different carbon atoms of propadiene are substituted by two configurationally and structurally identical groups, each containing one or more chiral centers (e.g. **7**).



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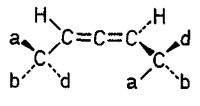

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M. V. Mavrov, V. F. Kucherov, *Usp. Khim.* **36**, 553 (1967).
M. Y. Lukina, *Usp. Khim.* **32**, 1425 (1963).
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D. R. Taylor, *Chem. Rev.* **67**, 317 (1967).
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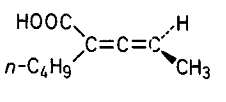
R. S. Cahn, C. K. Ingold, V. Prelog, *Angew. Chem.* **78**, 413 (1966); *Angew. Chem. Internat. Edit.* **5**, 385 (1966).

[3] M. Raban, K. Mislow, *Topics in Stereochemistry* **2**, 199 (1967).

Both asymmetric and dissymmetric allenes can exist in two enantiomeric forms. The configurational symbol of each enantiomer is assigned on the basis of the configurational nomenclature of Cahn, Ingold, and Prelog[2]. For example, the enantiomer **8** is viewed along the axis of the molecule and represented in the following projection.



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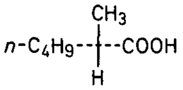


$$n\text{-}C_4H_9\text{--}\overset{CH_3}{\underset{H}{|}}\text{--}COOH$$

Since, by virtue of the sequence rule[2], the substituents located on the vertical axis take precedence over groups located on the horizontal axis, the precedence order is:

$$CH_3 > H > COOH > n\text{-}C_4H_9$$

Therefore, the enantiomer **8** has the (*S*)-configuration.

The definition of optical purity, its precise significance, and the general methods employed for its determination have been discussed elsewhere[3]. However, it is worthy of mention that, if the determination of the optical purity of a compound B* has been performed by chemically relating B* to a reference substance A* for which the relationship between the value of the rotatory power and optical purity is known, the optical purity determined can represent a "true", "minimum", or "maximum" value, depending on the determination procedure used.

A "true" value is obtained if B* is related to A* by reactions involving negligible racemization. However, if B* has been obtained from A* by reactions involving partial racemization, the value of the rotatory power of B* should not be referred to the optical purity of A*, but to one of lower value. Therefore, if the same optical purity as A* is attributed to B*, it must be specified that this value is a "maximum" optical purity.

If B*, of unknown optical purity, has been converted into A* by reactions which can involve partial racemization, the optical purity determined for B* is "minimum", since it is inclusive of the racemizations involved in converting B* into A*.

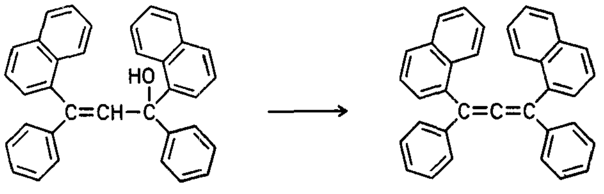
1. Naturally Occurring Chiral Allenes

The presence of an optically active allene in Nature was first shown[4] in 1952. It was later recognized that many other optically active allenes occur in natural products, principally amongst fungal metabolites, pigments of brown algae and sea urchins, diatoms, and leaves.

Most of the chiral compounds so far isolated (Table 1) can be subdivided into two classes. One class includes the diyne-allene grouping —C≡C—C≡C—CH=C=CH—; the other is represented by the carotenoid pigments.

2. Asymmetric Synthesis of Chiral Allenes

In 1935, Maitland and Mills[17] confirmed the van't Hoff prediction[18] of the existence of two enantiomeric forms for an unsymmetrically substituted allene by dehydrating racemic **9** with (+)-camphor-10-sulfonic acid to obtain the first optically active allene. The reduction product was shown to be a "feebly dextrorotatory" 1,3-bis-[1-naphthyl]-1,3-diphenylallene (**10**). After recrystallization until no change in the melting point was observed, the rotatory power of **10** was $[\alpha]_{5461}^{17}$: +437 (benzene).



9 **10**

A similar value for the rotatory power was obtained for (−)-**10** prepared using (−)-camphor-10-sulfonic acid[17].

The fact that simple recrystallizations led to a large increase of the value of the rotatory power of **10** demonstrated, however, that the product directly obtained from the dehydration process was predominantly a racemic mixture only partially enriched in one enantiomer.

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[13] G. Galasko et al., *J. Chem. Soc.* [C] **1069**, 1264.

[14] J. Cholnoky et al., *J. Chem. Soc.* [C] **1969**, 1256.

[15] H. W. S. Sprecher, R. Maier, M. Barbier, R. T. Holman, *Biochemistry* **4**, 1856 (1965).

[16] N. J. Antia, *Can. J. Chem.* **43**, 302 (1965).

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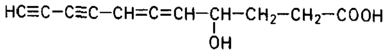
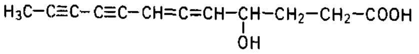
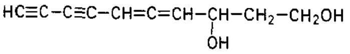
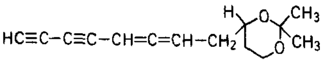
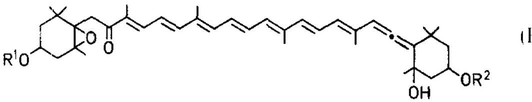
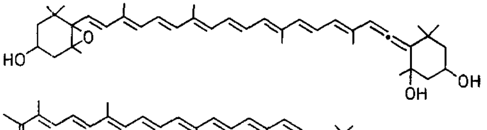
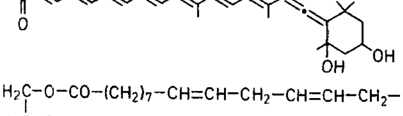
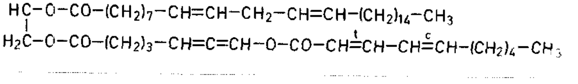
P. Maitland, W. H. Mills, *J. Chem. Soc.* **1936**, 987.

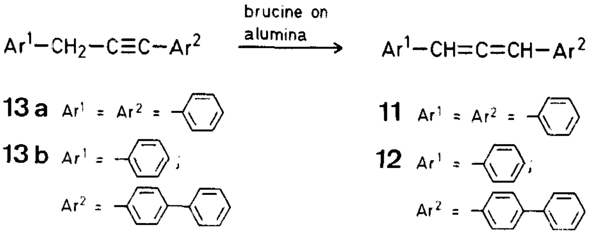
Table 1. Naturally Occurring Chiral Allenes

Formula	Trivial Name	$[\alpha]_D$	References
$HC\equiv C-C\equiv C-CH=C=CH-CH\overset{c}{=}CH-CH\overset{t}{=}CH-CH_2-COOH$	mycomycin	−130	4
 $HC\equiv C-C\equiv C-CH=C=CH-CH(OH)-CH_2-CH_2-COOH$	nemotinic acid	+380	5
 $H_3C-C\equiv C-C\equiv C-CH=C=CH-CH(OH)-CH_2-CH_2-COOH$	odyssic acid	+360	5
$HC\equiv C-C\equiv C-CH=C=CH-CH_2-COOCH_3$		+285	6
$HC\equiv C-C\equiv C-CH=C=CH-CH_2-CH_2OH$	marasin	+, −385	6, 7
$H_3C-C\equiv C-C\equiv C-CH=C=CH-CH_2-CH_2OH$		+340	8
$HC\equiv C-C\equiv C-CH=C=CH-CH_2OH$		−380	8
$HC\equiv C-C\equiv C-CH=C=CH-CH_2-CH_2-CH_2OH$		−290	8
$HC\equiv C-C\equiv C-CH=C=CH-(CH_2)_3-CH_2OH$		−180	8
 $HC\equiv C-C\equiv C-CH=C=CH-CH(OH)-CH_2-CH_2OH$		−210	8
		210	8
$H_3C-(CH_2)_{10}-CH=C=CH-(CH_2)_3-COOH$	laballenic acid	−47.3	9
$H_3C-(CH_2)_6-CH_2-CH=C=CH-CH\overset{t}{=}CH-COOH$		−128	10
 (R¹ = H, R² = H, Ac)		[a]	11, 12, 13
	neoxanthin	[b]	14
			13
		−21.9	15

[a] Optical activity has been demonstrated for the colorless perhydro derivative. The optical rotatory dispersion properties of this compound (R¹ = H, R² = Ac) have been reported[16].

[b] The optical rotatory dispersion curve of all-*trans*-neoxanthin between 350 and 200 nm is reported in Ref.[14].

Subsequently, Jacobs and Dankner[19] carried out the partial asymmetric synthesis of 1,3-diphenylallene (**11**) and 1-(*p*-biphenylyl)-3-phenylallene (**12**) by prototropic rearrangement of **13a** and **13b**, respectively, with alumina impregnated with brucine.



$$Ar^1-CH_2-C\equiv C-Ar^2 \xrightarrow{\text{brucine on alumina}} Ar^1-CH=C=CH-Ar^2$$

However, **11**, $[\alpha]_D^{23}$ +2.48, and **12**, $[\alpha]_D^{24}$ +8.57, had very low optical purity.

Asymmetric synthesis with unknown stereoselectivity was also realised in the reaction between the carboxylic acid chlorides **14a, b** and 1-alkoxycarbonylethylidenephosphoranes **15**, in which the alkyl residue was derived from (−)-menthol (**16a**) and octan-2-ol (**16b**), respectively[20].

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[18] J. H. vant'Hoff, *La Chimie dans l'Espace*, P. M. Bazendijk, Rotterdam, 1875, p. 29.

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[21] R. J. D. Evans, S. R. Landor, J. P. Regan, *Chem. Commun.* **1965**, 397.

[22] S. R. Landor, B. J. Miller, J. P. Regan, A. R. Tatchell, *Chem. Commun.* **1966**, 585.

[23] S. R. Landor, N. Punja, *Tetrahedron Lett.* **1966**, 4905.

[24] W. L. Waters, M. C. Caserio, *Tetrahedron Lett.* **1966**, 5233.

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L. Porri, R. Rossi, G. Ingrosso, *Tetrahedron Lett.* **1971**, 1083.

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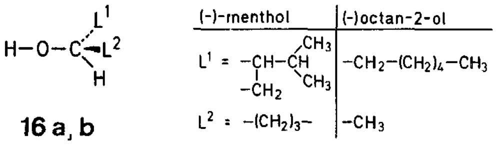
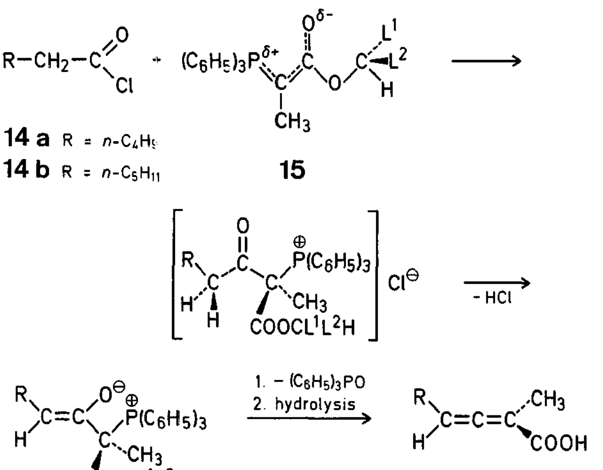
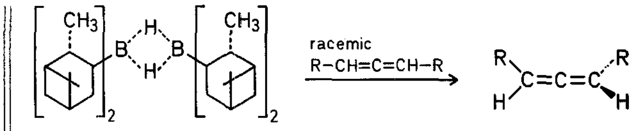

16 a, b


14 a R = n-C₄H₉
14 b R = n-C₅H₁₁
15

17 a R = n-C₄H₉, $[\alpha]_D^{22}$: -4.1 to -4.9
17 b R = n-C₅H₁₁, $[\alpha]_D^{22}$: -3.3 to -5.1

Landor et al.[21] demonstrated that optically active allenic alcohols may be obtained by assymmetric reduction of 1-hydroxyalk-2-en-4-ynes with lithium dimenthoxyaluminum hydride (**18**). The same optically active alcohols, but of opposite rotatory sign, and many others (Table 2) were later prepared by reduction using lithium aluminum hydride-3-O-benzyl-1,2-O-cyclohexylidene-α-D-glucofuranose complex (**19**)[22,23]. This reagent apparently displays a higher degree of stereoselectivity.

A simple one-step method for the partial resolution of racemic allenic hydrocarbons was developed by Caserio et al.[24,25]. By treating (+)-*sym*-tetraisopinocampheyldiborane (**20**) with an excess of racemic 2,3-pentadiene (**21**) or **11**, the recovered allene was enriched in one enantiomer.



20

(-)-**21** R = CH₃
(-)-**11** R = C₆H₅

The level of asymmetric induction, which was found to be very sensitive to the reaction conditions[24,25], compares favorably with that obtained by Jones et al.[26] (Section 4.).

We improved[27] the procedure of Caserio, obtaining for **21** a rotatory power value of $[\alpha]_D^{25}$: ~ −21 (neat) in several runs. After four successive asymmetric hydroboronations, (−)-**21** having $[\alpha]_D^{25}$: −78.84 (neat) was obtained. Further hydroboronations did not increase significantly the rotatory power of **21**.

(−)-Penta-2,3-diene[27]:
Boron trifluoride diglymate is prepared from boron trifluoride etherate (28.6 ml, 0.225 mol) and diglyme (60 ml) purified by several distillations from sodium and then from lithium aluminum hydride. This solution, after careful removal of ether under vacuum at 0°, is added slowly to a stirred solution of (−)-α-pinene (71.2 ml, 0.499 mol; $[\alpha]_D^{25}$: −55.0) and sodium borohydride (7.20 g, 0.190 mol) in diglyme (170 ml). The reaction mixture is allowed to stand for 15 hr at 0°, and then racemic penta-2,3-diene (36 ml, 0.371 mol) is rapidly added to the stirred borane mixture at 0°. The mixture is stirred for a further 4 hr at 0°, and the volatile components are removed at 25°; yield: 10.8 ml (30%) of (−)-penta-2,3-diene (99% pure by G.L.C.); $[\alpha]_D^{25}$: −21.0 (neat).

The procedure of Caserio[28] to prepare (−)-1,3-diphenylallene (**11**) was also modified. In a typical run, (−)-**11** of rotatory power $[\alpha]_D^{25}$: −231 (chloroform) was obtained. After three successive recrystallizations from pentane at −60°, the product had $[\alpha]_D^{25}$: −1137 (chloroform). This value is even higher than that reported by Jones et al.[26]: $[\alpha]_D^{25}$: +1020 (ethanol).

Table 2. Chiral Allenic Alcohols Obtained by Reduction of 1-Hydroxy-alk-2-en-4-ynes, -alk-2-ene-4,6-diynes, or -alk-2-ene-4,6,8-triynes with **18** or **19**

Reducing Agent	Unsaturated Alcohol	Allenic Alcohol	$[\alpha]_D$	References
18	1-hydroxyhex-2-en-4-yne	1-hydroxyhexa-3,4-diene	+ 8.3	21
18	1-hydroxyhept-2-en-4-yne	1-hydroxyhepta-3,4-diene	+ 2.3	21
19	1-hydroxyhex-2-en-4-yne	1-hydroxyhexa-3,4-diene	− 10	22
19	1-hydroxyhept-2-en-4-yne	1-hydroxyhepta-3,4-diene	− 8.9	22
19	1-hydroxynon-2-en-4-yne	1-hydroxynona-3,4-diene	− 7.4	22
19	1-hydroxy-8,8-dimethylnon-2-ene-4,6-diyne	1-hydroxy-8,8-dimethylnona-3,4-dien-6-yne	− 12.5	22
19	1-hydroxy-7-phenylhept-2-ene-4,6-diyne	1-hydroxy-7-phenylhepta-3,4-diene	− 3.1	22
19	1-hydroxynon-2-ene-4,6,8-triyne	marasin	− 26.6	22
19	1-hydroxydec-2-ene-4,6,8-triyne	9-methylmarasin	− 11.3	22
19	1-hydroxyhexadec-2-en-4-yne	1-hydroxyhexadeca-3,4-diene	− 4.4	23

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[29] H. Nozaki, T. Aratani, R. Noyori, *Tetrahedron Lett.* **1968**, 2087.

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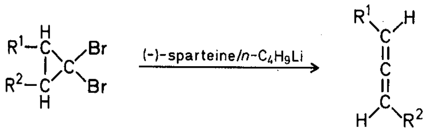
(–)-1,3-Diphenylallene:

Anhydrous tetrahydrofuran (8 ml) and (–)-α-pinene (2.3 g, 17.7 mmol) are placed in a 50 ml flask. Through the cold (0°) solution is passed a current of borane "externally" generated from boron trifluoride etherate (1.32 g, 9.3 mmol), sodium borohydride (0.270 g, 7.14 mmol), and diglyme (12 ml). The reaction mixture is maintained for 3 hr at 0°, then the solvent and excess α-pinene are removed by evaporation under vacuum. The residual light yellowish syrupy mass is dissolved in pentane (10 ml) and divided into two portions. Each portion is then eluted from silica gel in a 30 × 12 cm column with pentane (450 ml); yield: 0.76 g (33%) of (–)-1,3-diphenylallene; $[\alpha]_D^{25}$: –231 (c = 0.432, chloroform).

A new partial asymmetric synthesis of cyclic and acyclic allenes has been recently reported[29,30]. *gem*-Dibromides **22a, d** react with an equimolar mixture of (–)-sparteine and butyllithium to give optically active cyclotrideca-1,2-diene (**23**), cyclonona-1,2-diene (**24**), and 1-phenyl-3-methylallene (**25**), respectively.

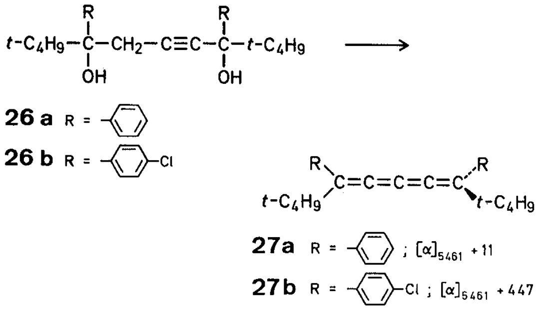


22a $R^1, R^2 = -(CH_2)_{10}$ *cis*	**23** $R^1, R^2 = -(CH_2)_{10}-$	;	$[\alpha]_D$ +1.4
22b $R^1, R^2 = -(CH_2)_{10}$ *trans*	**23** $R^1, R^2 = -(CH_2)_{10}-$	;	$[\alpha]_D$ –2.8
22c $R^1, R^2 = -(CH_2)_6$ *cis*	**24** $R^1, R^2 = -(CH_2)_6-$	;	$[\alpha]_D$ +1.9
22d $R^1 = C_6H_5$, $R^2 = CH_3$ *trans*	**25** $R^1 = C_6H_5$, $R^2 = CH_3$	;	$[\alpha]_D$ +2.0

The stereoselectivity of these reactions is probably very low. In fact, compound **24**, which in this synthesis has $[\alpha]_D$: +1.9 has been obtained by other means with a rotatory power as high as $[\alpha]_D^{25}$: +170–175 (dichloromethane)[31] (Section 6).

The asymmetric transformation of **22** into **23** was also accomplished by reaction of **22a, b** with chromium(II) (+)-tartrate[29,30]. However, in this case the rotatory power values for **23** were even lower than those obtained for **23** in the reaction with (–)-sparteine and butyllithium.

A group of Japanese workers reported the preparation of optically active 1,5-di-*t*-butyl-1,5-diphenylpentatetraene (**27a**) and 1,5-bis-[4-chlorophenyl]-1,5-di-*t*-butylpentatetraene (**27b**) by dehydratation of the acetylenic glycols **26a, b** with (+)-bromocamphorsulfonic acid[32].



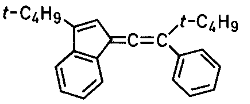
26a R = phenyl

26b R = 4-chlorophenyl

27a R = phenyl ; $[\alpha]_{5461}$ +11

27b R = 4-chlorophenyl ; $[\alpha]_{5461}$ +447

However, the product obtained from **26a** was later shown[33] to be 1-(3-*t*-butylindenylidene)-3,3-dimethyl-2-*cis*-phenyl-1-butene (**28**), not **27a**.



28

3. Resolution by Formation of Diastereoisomers[34]

Most of the racemic allenic compounds resolved by formation of diastereoisomeric salts are carboxylic acids. Various naturally occurring optically pure alkaloids have been used as resolving agents. In Table 3 are summarized the essential data of these resolutions. Details of the partial resolution of **31** are given in the following experiment.

Partial Resolution of Pentadienedioic Acid[37]**:**

A solution of racemic pentadienedioic acid (0.2 g, 1.56 mmol) in ether (32 ml) is slowly added to a solution of quinine (0.50 g, 1.55 mmol) in ether (100 ml). The colorless salt is isolated by filtration and dried under vacuum; yield: 0.64 g (91%); $[\alpha]_D$: –141. Trituration of the salt (0.61 g) with water gives cream-colored crystals (0.31 g), $[\alpha]_D$: –167, which are recrystallized by dissolving in a minimum amount of methanol and adding water until tan crystals (0.23 g) appear. This material is dissolved in aqueous methanol and aqueous sodium carbonate is added to pH 9. The resultant milky precipitate of quinine is removed by extraction with chloroform. Then, the pH of the solution is adjusted to 2 by the addition of 7 *M* sulfuric acid, and pentadienedioic acid is extracted with 6 portions of ether. The dried ethereal solution yields crystalline pentadienedioic acid (0.025 g); $[\alpha]_D$: –104.

The optical purity of acids **29–32** is unknown. However, the rotatory powers of **33–37** correspond to optically pure compounds[39] (Section 6.).

A method involving the formation of diastereomeric platinum(II) complexes, starting from *trans*-dichloro-(ethylene)-(optically active amine)-platinum(II) and *trans*-cycloalkenes has recently been applied[31] to the resolution of racemic cyclonona-1,2-diene (**24**). Diene **24**, $[\alpha]_D^{24}$: –61.6 (chloroform), was isolated by treatment of the complex

$$(\pm)\text{-}C_9H_{14}\cdot PtCl_2\cdot(+)\text{-}C_6H_5\text{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}\text{-}NH_2$$

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[31] A. C. Cope, W. R. Moore, R. D. Bach, H. J. S. Winkler, *J. Amer. Chem. Soc.* **92**, 1243 (1970).

[32] M. Nakagawa, K. Shingū, K. Naemura, *Tetrahedron Lett.* **1961**, 802.

[33] R. Kuhn, B. Schulz, *Angew. Chem.* **74**, 292 (1962).

[34] For a recent review on the methods of optical resolution, see P. H. Boyle, *Quart. Rev.* **25**, 323 (1971).

[35] E. P. Kohler, J. T. Walker, M. Tishler, *J. Amer. Chem. Soc.* **57**, 1743 (1935).
The enantiomeric methyl esters of this acid have $[\alpha]_D$: –48.8 and +49.3, respectively: E. P. Kohler, W. J. Whitcher, *J. Amer. Chem. Soc.* **62**, 1489 (1940).

[36] L. Crombie, P. A. Jenkins, *Chem. Commun.* **1967**, 870.

Table 3. Resolution of Allenic Carboxylic Acids by Formation of Diatereomers with Alkaloids

Resolving Agent	Allenic Carboxylic Acid		References
	Structure	$[\alpha]_D$	
Brucine	1,3-diphenyl-3-(1-naphthyl)-allenecarboxylic acid (**29**)[a]	+, −29.5	35
Quinine	2-methylbuta-2,3-dienoic acid (**30**)	+, −36.1	36
Quinine	pentadienoic acid (glutinic acid) (**31**)	−104	37
Strychnine	2-butylpenta-2,3-dienoic acid (**32**)	−30.69	38
Cinchonidine	4-phenylbuta-2,3-dienoic acid (**33**)	+420	39
Cinchonidine	4-phenylpenta-2,3-dienoic acid (**34**)	+318	39
Cinchonidine	4-phenylhexa-2,3-dienoic acid (**35**)	−280	39
Cinchonidine	5-methyl-4-phenylhexa-2,3-dienoic acid (**36**)	+205	39
Cinchonidine	5,5-dimethyl-4-phenylhexa-2,3-dienoic acid (**37**)	+177	39

[a] The resolution was accomplished with the glycolic acid ester of this allenic acid[35].

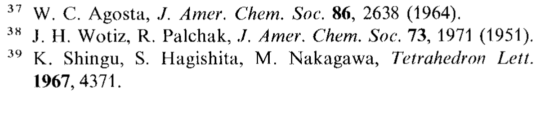
which had been enriched in the less-soluble diastereomer by thirteen recrystallizations, with aqueous sodium cyanide. The resultant **24** had an optical purity of ~**44**%[31,41] (Section 6.).

Although this method does not appear to be general, since its use is restricted by the requirement that the complexes must be crystalline solids capable of being fractionally recrystallized, it possesses the great advantage that it is independent of the presence of functional groups which can be used as resolving "handles".

Recently, the resolution of racemic **24** was achieved by asymmetric hydroboranation with **20**[82]. Partially resolved **24** having $[\alpha]_D$: +26 corresponded to ~15% optical purity. On the basis of the findings of Moore et al.[83], the *R* configuration was attributed to this compound (cf. Section 5., p. 36).

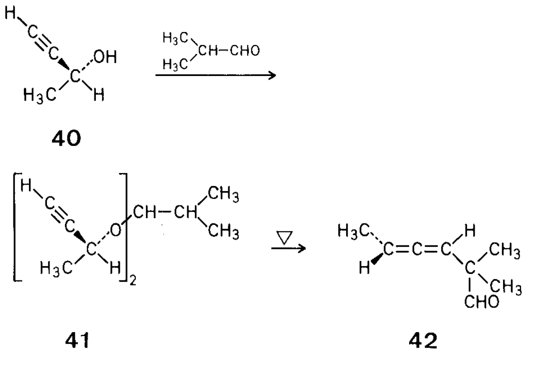
4. Synthesis from a Chiral Precursor Containing an Asymmetric Carbon Atom or Exhibiting Molecular Dissymmetry

The first stereospecific synthesis of a chiral allene from an optically active tetrahedral carbon compound was described by Landor et al.[42,43]. Alkyne **38**, $[\alpha]_D^{20}$: −0.83, and its corresponding enantiomer, react with thionyl chloride in boiling dioxane to give 1-chloro-3,4,4-trimethylpenta-1,2-diene (**39**), $[\alpha]_D^{20}$: −53.10 and +52.53, respectively. The optical purity of **39**, $[\alpha]_D^{20}$: ±50, was estimated to be 50–60%.



38 **39**

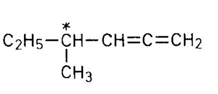
Jones, Loder, and Whiting[44] prepared (−)-2,2-dimethylhexa-3,4-dienal (**42**), α_D^{28} (l=1): −15.9, from **40**, α_D^{17} (l=1): +11.2, in the following manner.



40 **41** **42**

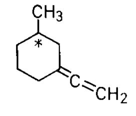
A discussion of the stereochemistry of the above two syntheses is given in Section 5.

Only three examples of asymmetric chiral allenes in which the asymmetry (and, therefore, the optical activity) is derived from the presence of an asymmetric carbon atom in the α or β position with respect to the allenic group have thus far been reported[45,46]. These are (*S*)(+)-4-methylhexa-1,2-diene (**43**), (*R*)-(−)-3-methyl-1-vinylidenecyclohexane (**44**), and (*S*)-(+)-5-methylhepta-1,2-diene (**45**).



$C_2H_5-\underset{CH_3}{\overset{*}{C}H}-CH=C=CH_2$

43



44

Allenes **43**, $[\alpha]_D^{25}$: +49.47 (neat), and **44**, $[\alpha]_D^{25}$: −47.6 (neat), were prepared according to the method of Doering, Moore, and Skattebøl[47] starting from (*S*)(+)-3-methylpent-1-ene, $[\alpha]_D^{25}$: +32.84 (neat), and (*R*)(−)-3-methyl-1-methylenecyclohexane [obtained from (*R*)-pulegone], $[\alpha]_D^{25}$: −47.76, respectively[45,46]. Allene **45**, $[\alpha]_D^{25}$: +9.49 (neat), was prepared by the stereospecific reaction of 3-bromo-

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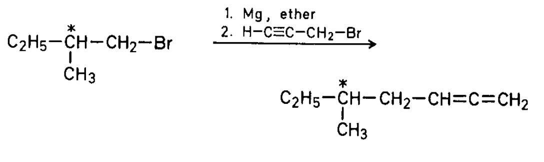
[37] W. C. Agosta, *J. Amer. Chem. Soc.* **86**, 2638 (1964).

[38] J. H. Wotiz, R. Palchak, *J. Amer. Chem. Soc.* **73**, 1971 (1951).

[39] K. Shingu, S. Hagishita, M. Nakagawa, *Tetrahedron Lett.* **1967**, 4371.

propyne with the magnesium derivative of (*S*)-1-bromo-2-methylbutane, $[\alpha]_D^{25}$: +4.00 (optical purity: 95.1%)[46].

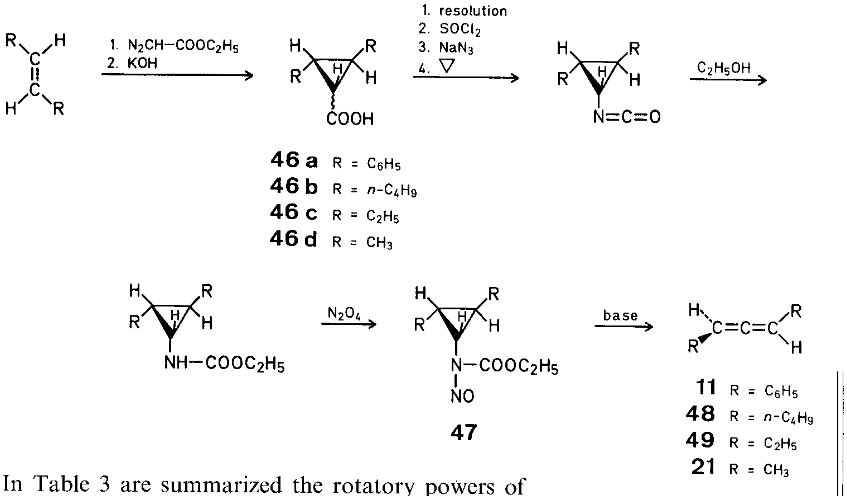


45

A useful general method for the synthesis of chiral allenes was developed by Walbrick, Jones, et al.[26,48]. Optically active *trans*-2,3-dialkyl(or -aryl)cyclopropanecarboxylic acids were prepared by addition of ethyl diazoacetate to the appropriate *trans*-olefin, followed by hydrolysis and optical resolution. These optically active acids were converted into the corresponding ethyl carbamates via the acid chlorides, acid azides, and isocyanates. Nitrosation and treatment with strong bases yielded the corresponding chiral 1,3-dialkyl(or -aryl) allenes.

The stereochemistry of the ring opening of cyclopropane-N-nitrosocarbamate **47** with bases was found to be dramatically affected by the nature of the reaction solvent[49]. Thus, (+)-**11** obtained from the reaction in cyclohexane, cyclohexene, benzene, *t*-butanol, and methanol was found to have a specific rotatory power of 686 ±30, 607 ±30, 350±30, and 197 ±30, respectively[49].

The two enantiomers of another dissymmetric aliphatic allene, 1,3-di-*t*-butylallene (**53**), were synthesized by Borden and Corey[50] according to the following reaction sequence: racemic **50** was esterified with (+)-camphor-10-sulfonyl chloride and the corresponding ester recrystallized to separate the two diastereomers **51** and **52**. Reduction of **51**, $[\alpha]_{578}^{22}$: −27.8 with lithium aluminum hydride in refluxing tetrahydrofuran afforded (+)-**53**, $[\alpha]_{578}^{22}$: +34.6 (benzene), mixed with the isomeric acetylene **53a**. Analogously, the reaction of **52**, $[\alpha]_{578}^{22}$: +91.5, gave (−)-**53**, $[\alpha]_{578}^{22}$: −39.8 (benzene).

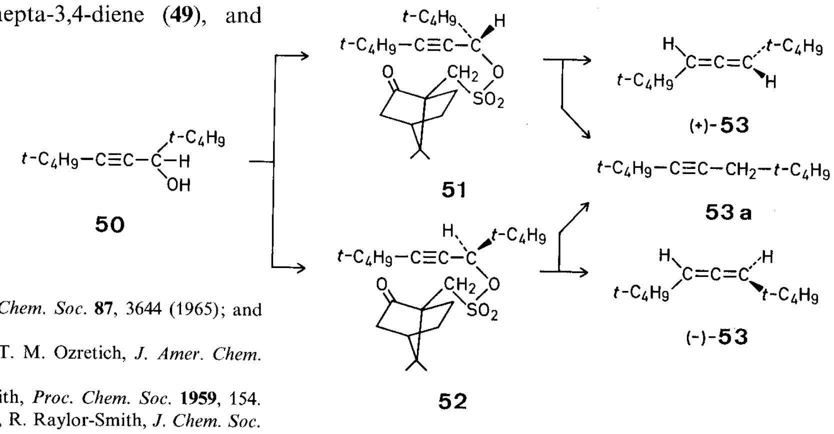


46a R = C6H5
46b R = *n*-C4H9
46c R = C2H5
46d R = CH3

47

11 R = C6H5
48 R = *n*-C4H9
49 R = C2H5
21 R = CH3

In Table 3 are summarized the rotatory powers of the cyclopropanecarboxylic acids **46a–d** and of the corresponding products 1,3-diphenylallene (**11**), undeca-5,6-diene (**48**), hepta-3,4-diene (**49**), and penta-2,3-diene (**21**).



50 **51** **52** (+)-**53** **53a** (−)-**53**

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[40] A. C. Cope et al., *J. Amer. Chem. Soc.* **87**, 3644 (1965); and references therein.

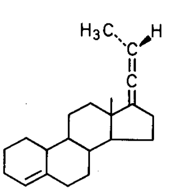
[41] W. R. Moore, R. D. Bach, T. M. Ozretich, *J. Amer. Chem. Soc.* **91**, 5918 (1969).

[42] S. R. Landor, R. Taylor-Smith, *Proc. Chem. Soc.* **1959**, 154.

[43] R. J. D. Evans, S. R. Landor, R. Raylor-Smith, *J. Chem. Soc.* **1963**, 1506.

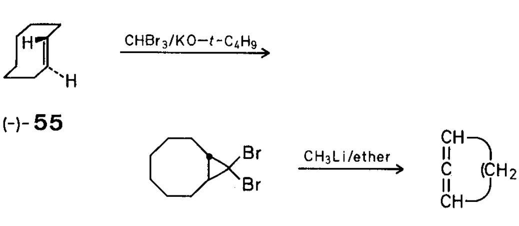
Allene (−)-**53** was also prepared by reduction of the tosylate ($[\alpha]_{578}^{22}$: +64.0) of optically pure (+)-**50** with various hydride reagents. The highest value for the rotatory power of **53**, $[\alpha]_{578}^{22}$: −72.8 (benzene), was obtained for a sample prepared by reduction with lithium dimethoxyaluminum hydride. Finally, optically active **53** was also obtained by reaction of (+)-**50** with lithium aluminum hydride in the presence of aluminum chloride. However, the sign of rotation of the allene was found to be dependent on the amount of aluminum chloride used[50].

The reduction of a propargylic alcohol with lithium aluminum hydride in tetrahydrofuran was also used to prepare 21-methyl-19-nor-4,17,20-pregnatriene (**54**), $[\alpha]_D$: +142 (chloroform), from 17β-hydroxy-17α-propynyl-4-estrene[51].



54

Cope et al.[31] have described an example of stereospecific synthesis of a chiral dissymmetric allene from a chiral dissymmetric compound. (*R*)(−)-*trans*-cyclooctene (**55**) was converted into (+)-cyclonona-1,2-diene (**24**) by a More-Skattebøl-Doering synthesis. Allene (+)-**24** had optical purity higher than that of **24** obtained through resolution[31].



(−)-**55** (+)-**56** (+)-**24**

(+)-Cyclonona-1,2-diene[31]:

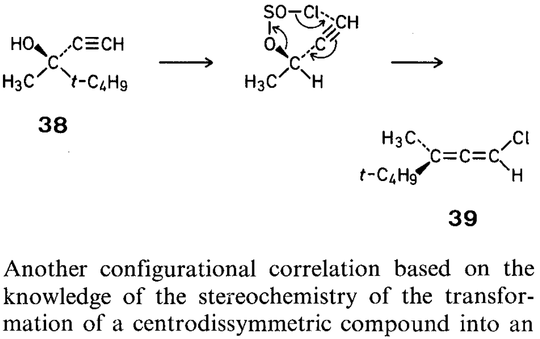
(+)-*9,9-Dibromo*-trans-*bicyclo[6.1.0]nonane* (**56**); To a stirred solution of potassium *t*-butoxide (3.7 g, 0.033 mol) in (−)-*trans*-cyclooctene (3.3 g, 0.030 mol), $[\alpha]_D^{25}$: −437 (neat), and pentane (75 ml) maintained at 0° under nitrogen is added dropwise distilled bromoform (8.3 g, 0.033 mol). Water is added and the aqueous layer is extracted with pentane (3 × 75 ml). The combined organic layers are dried with sodium sulfate. The solvent is evaporated and the colorless solid residue recrystallized from methanol; yield: 4.1 g (48%); m.p. 51.5–53°; $[\alpha]_D^{25}$: +44.2 (c = 2.5, dichloromethane).

(+)-*Cyclonona-1,2-diene:* To a solution of compound **56** (3.5 g, 1.24 mmol) in ether (75 ml) maintained at 0° under nitrogen is added a 1.6 *M* solution (9 ml) of methyllithium in ether. Water is added, the aqueous layer is shaken with ether, and the combined ether extracts are dried with sodium sulfate. The solvent is evaporated and the residue subjected to bulb-to-bulb distillation; yield: 1.35 g (89%); $[\alpha]_D^{25}$: +138 (c = 3.6, dichloromethane).

5. Determination of Absolute Configuration

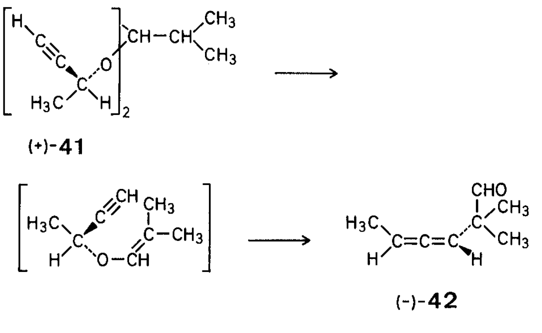
This section is exclusively devoted to methods reported in the literature to establish the absolute configuration of chiral allenes containing no asymmetric carbon atom. In the case of asymmetric allenes such as **43**, **44**, and **45**, the relationship between the sign of optical rotation and absolute configuration is immediately obvious from the method of preparation[45,46] (Section 4.).

Most determinations of absolute configuration of chiral allenes involve suitable chemical correlations of these with "centrodissymmetric" molecules of known configuration[52]. For example, (+)-1-chloro-3,4,4-trimethylpenta-1,2-diene (**39**) was correlated with (*S*)(+)-3-hydroxy-3,4,4-trimethylpent-1-yne[53] (**38**) by synthesizing the former from the latter[42,43] (Section 4.). Since this stereospecific synthesis presumably proceeds through a cyclic S_Ni mechanism, the chlorine atom would be expected to approach from the side on which the hydroxy group is situated. Thus, (+)-**39** should have (*R*)-configuration[54].



38 **39**

Another configurational correlation based on the knowledge of the stereochemistry of the transformation of a centrodissymmetric compound into an asymmetric chiral allene was achieved by Jones[44]. Pyrolysis of the dextrorotatory acetal **41**, which is of known configuration since it is obtained from (*R*)(+)-3-hydroxybut-1-yne (**40**), to dienal **42**, involves a stereospecific Claisen-type rearrangement of an intermediate enol ether. This reaction proceeds through a cyclic transition state requiring the attachment of the olefinic carbon and detachment of the oxygen atom on the same side of the molecule. It was, therefore, concluded that (−)-**42** has (*R*)-configuration[44].



(+)-**41** (−)-**42**

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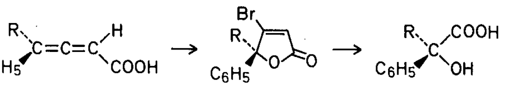
[44] E. R. H. Jones, J. D. Loder, M. C. Whiting, *Proc. Chem. Soc.* **1960**, 180.

Table 4. Specific Rotatory Powers of Cyclopropanecarboxylic Acids **46a–d** and the Allenes Prepared from them[26]

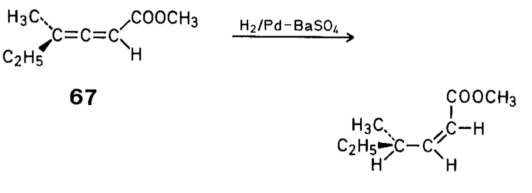
Cyclopropanecarboxylic Acids	$[\alpha]_D$	Allene	$[\alpha]_D^{25}$
46a	−20.8 (95% ethanol)	**11**	+459 (hexane)
46b	− 2.78 (95% ethanol)	**48**	− 7.5 (CCl_4)
46c	+ 1.74 (95% ethanol)	**49**	+ 11.2 (CCl_4)
46d	−10.0 (ethanol)	**21**	+ 25.3 (CCl_4)

Conversely, Shingu, Hagishita, and Nakagawa[39] assigned absolute configuration to allenes **33**–**37** by converting these acids into centrodissymmetric compounds of known chirality. Treatment of compounds **33**–**37** with bromine in carbon tetrachloride gave the optically active β-bromolactones **57**–**61**, respectively, which were converted into the corresponding hydroxy acids **62**–**66**, all of (*S*)-configuration[55–58], by permanganate oxidation and subsequent hydrolysis.



(+)-**33** R = H **57** (+)-**62** R = H
(+)-**34** R = CH_3 **58** (+)-**63** R = CH_3
(−)-**35** R = C_2H_5 **59** (−)-**64** R = C_2H_5
(+)-**36** R = *i*-C_3H_7 **60** (+)-**65** R = *i*-C_3H_7
(+)-**37** R = *t*-C_4H_9 **61** (−)-**66** R = *t*-C_4H_9

Crombie and Jenkins[36] developed another method for determining the absolute configuration of unsubstituted chiral allenes. Partial hydrogenolysis of methyl (−)-4-methylhexa-2,3-dienoate (**67**), $[\alpha]_D$: −29.4, using palladium on barium sulfate, gave a mixture of esters from which **68**, $[\alpha]_D$: −9.8, was separated. Hydrogenation of **68** gave[59] methyl (−)-4-methylhexanoate (**69**), $[\alpha]_D^{21}$: −7.4 (optical purity: 72.7%). Since the absolute configuration of (−)-**69** was known[59] to be (*R*), the absolute configuration of (−)-**67** is also (*R*), assuming a *cis* mechanism for the partial hydrogenation. In confirmation, oxidative degradation of (+)-**68**, $[\alpha]_D$: +5.5, obtained from (+)-**67**, $[\alpha]_D^{24}$: +21.7, followed by esterification gave with partial racemization methyl (*S*)(+)-2-methylbutanoate, $[\alpha]_D^{23}$: +5.1 (optical purity: 21.3%)[60].



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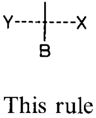
68

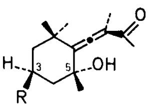
In 1965, Lowe[61] proposed a rule, subsequently developed by Brewster[62], which relates the absolute configuration of a chiral allene to the sign of its rotatory power at the sodium D-line. The rule states that if the most polarisable substituent of a chiral allene is placed uppermost in the vertical axis and the more polarisable of the two rear substituents in the horizontal axis is to the right, a clockwise screw pattern of polarisability will be obtained, and the enantiomer will be dextrorotatory; if the more polarisable of the two rear substituents is on the left hand side, the allene will be levorotatory.



Dextrorotatory if the polarisability order is A > B and X > Y.

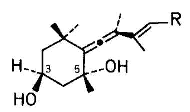
This rule has been useful in predicting the absolute configuration of many chiral synthetic[21,63] and "natural" allenes (e.g., laballenic acid, nemotinic acid, mycomycin, odyssic acid)[60]. However, (+)-cyclonona-1,2-diene does not conform to this rule[64].

The absolute configuration of natural allenic carotenoids such as fucoxanthin, neoxanthin, and their derivatives (Table 1) was successfully established in the following manner. An X-ray analysis of **69b**, prepared from the optically active degradation product (**69a**) of fucoxanthin demonstrated that the C-5 hydroxy group is *cis* to the allenic hydrogen atom and *trans* to both other oxygen functions[65]. Since an (*S*)-configuration seems probable at C-3 and C-3′ in fucoxanthin, neoxanthin, and their derivatives[11,13,14], such natural compounds should have the absolute configuration shown[65] in **70**.



69a R = $H_3C-CO-O-$

69b R = $Br-C_6H_4-CO-O-$



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[45] R. Rossi, P. Pino, *Chim. Ind. (Milano)* **48**, 961 (1966).

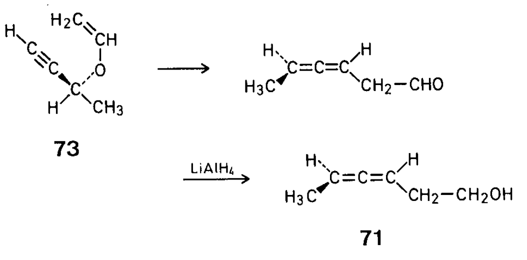
[46] P. Salvadori, R. Rossi, E. Chiellini, *Chim. Ind. (Milano)* **50**, 1365 (1968).

[47] W. E. von Doering, P. M. La Flamme, *Tetrahedron* **2**, 75 (1958);
W. R. Moore, H. R. Ward, *J. Org. Chem.* **27**, 4179 (1962);
L. Skattebøl, *Acta Chem. Scand.* **17**, 1683 (1963).

[48] W. M. Jones, J. W. Wilson, F. B. Tutwiler, *J. Amer. Chem. Soc.* **84**, 3309 (1963).

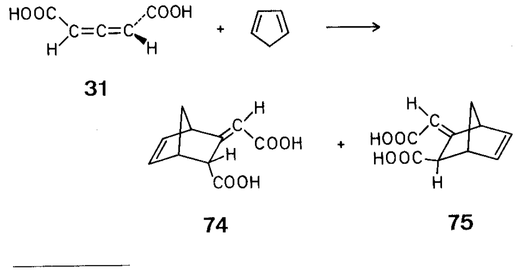
Allenes (+)-1-hydroxyhexa-3,4-diene (**71**) and (+)-1-hydroxyhepta-3,4-diene (**72**), obtained from the corresponding enynols by reduction with lithium dimenthoxyaluminum hydride (**18**), were predicted to possess (*S*)-configuration by considering the conformation of the thermodynamically more stable cyclic complex derived from **18** and 1-hydroxyhex-2-en-4-yne or 1-hydroxyhept-2-en-4-yne, respectively (Table 2). Analogously, the (*R*)-configuration was attributed to all levorotatory allenic alcohols reported in Table 2, either on the basis of examinations of models of the polymeric hydroxyallene aluminum monosaccharide complex formed in the reduction of the corresponding enynols with **19**, or on the basis of the Lowe-Brewster rule[22, 23].

The absolute configuration of (+)-**71** was confirmed[21] to be (*S*) by synthesis of (+)-**71** from (*S*)-(−)-3-hydroxybut-1-yne via Claisen-Cope rearrangement of the intermediate (*S*)-vinyl but-1-yn-3-yl ether (**73**).

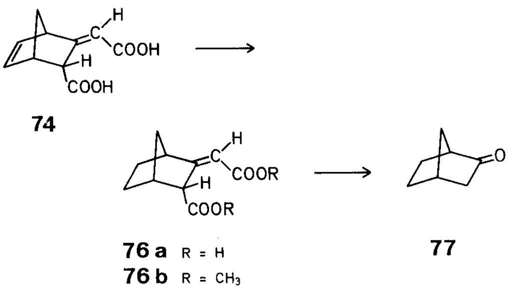


The Prelog rule[66] was employed by Tömösközi and Bestmann[20] to assign the (*S*)-configuration to allenic acids (−)-**17a** and (−)-**17b**, which were asymmetrically synthesized from carboxylic acid chlorides **14a** and **14b** and the 1-alkoxycarbonylethylidenephosphorane **15**. However, in the absence of other evidence, this assignment should be treated with caution.

A very ingenious method was devised by Agosta[37] to establish the absolute configuration of (−)-pentadienedioic acid (**31**, Table 3). Partially resolved (−)-**31** was treated with cyclopentadiene to give a mixture of two isomers (**74** and **75**), from which **74**, $[\alpha]_D$: +39, was separated.



Acid **74** was selectively hydrogenated to yield **76a**, and the corresponding dimethyl ester (**76b**) was transformed into crude norcamphor (**77**). Compound **77** was then converted into the corresponding 2,4-dinitrophenylhydrazone (**78**), $[\alpha]_D$: +9.



A parallel sequence starting from **75**, $[\alpha]_D$: −53, gave a 2,4-dinitrophenylhydrazone of opposite rotation, $[\alpha]_D$: −14.1. Since the 2,4-dinitrophenylhydrazone prepared from (+)-**77** is dextrorotatory and (+)-norcamphor has the absolute configuration shown[67] in **77**, (−)-pentadienedioic acid must have the (*R*)-configuration[68].

One highly successful determination of absolute configuration by physical methods was carried out by Mason and Vane[69]. By observing the U.V. and C.D. (circular dichroism) spectra of (+)-1,3-diphenylallene (**11**) and applying the coupled-oscillator method, they deduced that (+)-**11** has (*S*)-configuration. This in agreement with the results of Jones and Wilson[70], who analysed the stereochemical course of conversion of (−)-*trans*-2,3-diphenylcyclopropane carboxylic acid (**46a**) into (+)-**11** (Section 4.). Since this transformation proceeds by way of an intermediate diazocyclopropane and the stereochemistry of ring opening of this compound is controlled by the steric repulsion of the *trans* groups, a knowledge of the absolute configuration of the diazocyclopropane or of its precursor **46a**, allowed the assignment[70] of the absolute configuration of (+)-**11**.

Acid (−)-**46a** was then converted[70] into (−)-*trans*-1,2-diphenylcyclopropane (**79**) and finally into (1*R*; 2*R*)(−)-*trans*-2-phenylcyclopropanecarboxylic acid (**80**)[71]. Therefore, the (*S*)-configuration was assigned to (+)-**11**. Using a similar procedure, the (*S*)-configuration was assigned[72] to (+)-2,3-pentadiene (**21**) prepared from (+)-*trans*-2,3-dimethylcyclopropanecarboxylic acid (**46d**, Section 4.). This configuration for (+)-**21** was predicted by Brewster[62] and independently, on the basis of asymmetric hydroboronation, by Waters and Caserio[24, 25].

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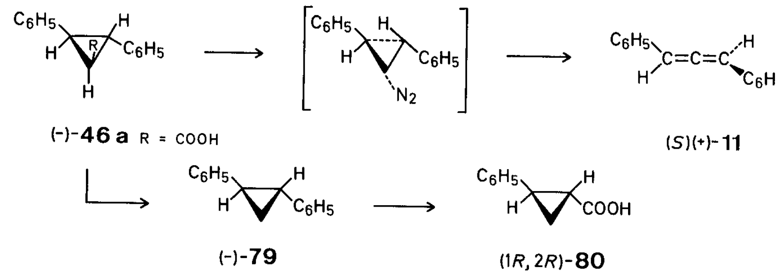


Recently, the C.D. data of some chiral allenes with established configuration, and the dynamic coupling theory of optical activity[73] have led to the proposition of a sector rule which predicts the stereochemical configuration of an allene on the basis of the Cotton effect associated with the lowest-energy absorption band of the allenic chromophore (220–250 nm)[64].

The C.D. data of (*S*)-**43**, (*R*)-**44**, and (*S*)-**45** are correctly predicted by this rule.

6. Determination of Optical Purity

Only a few reports of determinations of optical purity of chiral allenes have appeared. All the published examples deal with determinations relative to a reference substance. Absolute methods, such as those of Gil-Av[74] and Pirkle[75], have not so far been employed.

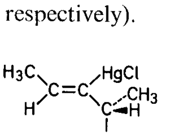
The relationship between rotatory power and optical purity of (+)-**43** and (+)-**45** was determined by converting these compounds into (*S*)-3-methylhexane (**81**) and (*S*)-3-methylheptane (**82**), respectively[45,46], and by comparing the rotatory powers of **81** and **82** with the maximum values reported in the literature for these paraffins, $[\alpha]_D^{25}$: +9.9 and +10, respectively.

Allene **43**, $[\alpha]_D^{25}$: +49.47, was thus found to be minimum 78.8% optically pure; compound **45**, $[\alpha]_D^{25}$: +4.20, is 95% optically pure.

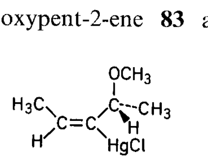
The maximum optical purity of (*R*)-**44**, $[\alpha]_D^{25}$: −47.60, was estimated[46] to be comparable to that of the (*R*)-pulegone used as a starting material (94–95%).

Shingu, Hagishita, and Nakagawa[39] established the minimum optical purity of allenic acids **33**, **34**, and **35** (Table 3) by converting these into the corresponding hydroxy acids **62**, $[\alpha]_D$: +151, **63**, $[\alpha]_D$: +36.5, and **64**, $[\alpha]_D$: −32 (Section 5.) and comparing the rotatory power values of the latter compounds with the highest values reported for these acids[78,79,80]. Hydroxy acids **62**, **63**, and **64**, and therefore also the allenic acids **33**, **34**, and **35** were thus determined to be optically pure[39].

An example of the determination of the minimum optical purity of chiral dissymmetric allenes was reported by Waters, Linn, and Caserio[81]. The reaction of (*R*)-penta-2,3-diene (**21**), $[\alpha]_D$: −15.9 (ether), with mercuric acetate and then with aqueous sodium chloride gave a mixture of *trans*- and *cis*-3-chloromercuri-4-methoxypent-2-ene **83** and **84**, respectively).



(−)-83



84

Reduction of (−)-**83** with sodium borohydride gave (−)-**85**, which was catalytically hydrogenated to (*S*)-2-methoxypentane (**85**), $[\alpha]_D$: +1,2 (chloroform). Compound (+)-**86** was also obtained by reduction of the acid phthalate of *trans*-(*S*)-(+)4-hydroxypent-2-ene $[\alpha]_D^{22}$: +22.0 (chloroform) (58% optically pure), methylation of the resultant (+)-**87** to (−)-**85**, $[\alpha]_D$: −54.2 (chloroform), and catalytic reduction of (−)-**84** to (+)-**86**, $[\alpha]_D$: +9.9 (chloroform).

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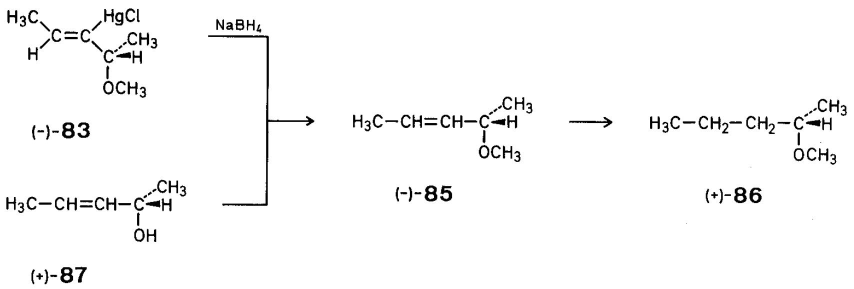
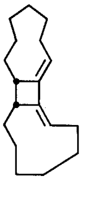


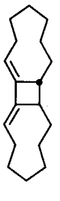
Assuming that conversion of either the dextrorotatory acid phthalate of **87** into (−)-**85**, or of (−)-**21** into (−)-**85** occurs without appreciable racemization, the optical purity of (−)-**21**, $[\alpha]_D$: −15.9, should[81] be 7%. This value is in fair agreement with that based on the maximum rotatory power calculated by Brewster[62] for (−)-**21** (9%).

Finally, Moore, Bach, and Ozretich[41] determined the maximum rotatory power of (+)-cyclonona-1,2-diene (**24**) by referring to results obtained in the dimerization of this compound; this corresponds to a determination of the optical purity of **24** prepared either through formation of diastereomeric platinum(II) complexes, or starting from (−)-*trans*-cyclooctene[31].

Dimerization of **24**, $[\alpha]_D^{25}$: +163 (dichloromethane), afforded **88**, **89**, and **90** in the ratio 0.43 : 12.82 : 86.73.



88



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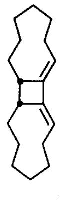

90

Compounds **88** and **89** are derived from dimerization of the two enantiomers of **24**, whereas **90** is obtained from the dextrorotatory enantiomer.

Assuming that the dimerization was 100% stereospecific and the relative rates of dimerization for either the two enantiomers of **24** or for the single dextrorotatory enantiomer were the same as for the racemic allene, it is possible to estimate[41] a maximum rotatory power value of $[\alpha]_D^{25}$: +170–175 (dichloromethane) for **24**.

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