The Chemistry of
THE ALLENES

Edited by
S. R. LANDOR

Volume 3
Stereochemical, Spectroscopic
and Special Aspects

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STEPHEN R. LANDOR

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Foreword

My first practical acquaintance with an allenic compound, although I was not to know it until many years later, was with one of the most intractable of the carotenoid pigments, fucoxanthin, at Manchester in 1937. Until the post-war years, to most of us the allenic structure was of theoretical stereochemical interest.

It was in 1874, in what can fairly be regarded as the most important individual publication in organic chemistry, that J. H. van't Hoff, then only 22, made far-reaching predictions about compounds containing cumulative ethylenic bonds, i.e.

$$\geq C{=}(C{=})_n C\leq$$

He discerned that in the series with an even-number of double bonds (where $n = 1,3,5$ etc) appropriately substituted compounds should exhibit asymmetry and hence be resolvable into optical isomers while in the odd-numbered series (where $n = 2,4$ etc) they should exhibit *cis-trans*-isomerism as with simple ethylenic compounds. The first of these was eventually proved more or less simultaneously by W. H. Mills and P. Maitland at Cambridge and by E. P. Kohler, J. T. Walker and M. Tishler at Harvard in 1935, whereas his second proposition had to wait another two decades for substantiation (R. Kuhn and K. L. Scholler, 1954).

Apart from the above the text books of the 1950's, which had little to relate even about acetylene chemistry, were even more reticent regarding allenes, Karrer mentioning only allene and dimethylallene. However, interest was deservedly aroused by Jacobs' (T. L. Jacobs, R. Akawie and R. G. Cooper, 1951) classical study of the prototropic rearrangement of alkynes and the isomeric allenes. For us, encountering allenic compounds in the course of synthetic studies, observation of the facile rearrangement of methyl but-3-ynoate with bicarbonate and the production of penta-3,4-dienol by lithium aluminium hydride reduction of pentenynol gave clear indications of the ubiquity and stability of these unfamiliar compounds. The facile detection of the allene system by its infrared absorption and its recognition in the remarkable fungal metabolite mycomycin, $C_{13}H_{10}O_2$, by W. D. Celmer and I. A. Solomons (1952) helped significantly to generate interest in this hitherto neglected combination of ethylenic unsaturation so that in the last quarter of a century developments have been continuous and considerable.

The results of work in the allene field are widely scattered through the literature and the time has surely come when they should be collected together in a convenient form to enable the fullest advantage to be taken of the knowledge that has been accumulated. Professor Stephen Landor became interested in allene chemistry whilst at Manchester in the early 1950's and he and his wife have contributed consistently and notably to this field, despite vicissitudes which would undoubtedly have deterred many less-enthusiastic spirits. He has built up a vast fund of knowledge and experience of the last 30 years and there is no one better qualified to produce a definitive work on the subject.

University of Oxford Sir Ewart R. H. Jones, F.R.S.

Preface

The number of publications involving allenes has increased from just a few in 1955 to about one hundred and fifty per annum in the seventies. A comprehensive monograph is long overdue and when I was approached by the publishers I readily agreed that Dr. P. D. Landor and I would write on Allenes. However, the phenomenal expansion of the field made it necessary to invite other authors, all experts specialising in different aspects of allene chemistry, to contribute if the work was ever to be completed. The book aims at comprehensive, yet critical coverage of the chemistry of allenes in a readily digestible form. We have emphasised the useful aspects of syntheses and reactions of allenes, the chemistry of natural and biologically active allenes and allenic intermediates in organic synthesis as well as applications of the stereochemistry and spectroscopic properties of allenes. The last chapter describes key experimental techniques which we feel any third year undergraduate should be able to apply successfully.

The volumes are intended to serve all chemists, experts and novices, academic and industrial alike and help them to include allenes in their research programmes. We shall be well satisfied if others feel, as we do, that they will fill an important gap in chemical knowledge.

The University of the West Indies,
Mona, Kingston, Jamaica.
January 1982

Stephen R. Landor

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CHAPTER 6

Stereochemistry of Allenes

WOLFGANG RUNGE

Structural chemistry predicts that allenes are nonplanar with the substituents lying in perpendicular planes.[1] This has been verified experimentally for various types of allenes. Consequently, allenes may become chiral through an appropriate arrangement of (achiral) ligands on the four ligand sites of the allenic molecular skeleton. The configurational stability of allenes is well known,[1] and therefore such chiral allenes can be isolated under normal laboratory conditions. It is the intention here to summarize stereochemical aspects of the chirality of allenes. Starting from structural features that give rise to chiral allenes, this chapter describes methods for the determination of absolute configurations of the various kinds of chiral allenes from chiroptical properties, including molar rotations $[\phi]_D^{25}$ at the wavelength of the sodium D line, optical rotatory dispersion (o.r.d.) $[\phi]_\lambda^{25}$ for different wavelengths, or circular dichroism (c.d.) $\Delta\varepsilon$ of electronic bands. Furthermore, possibilities for determining optical purity (o.p.) or enantiomeric excess (e.e.),[1] of molecular ensembles having given optical rotations, are discussed.

The central topic of this chapter, however, is concerned with an overview covering the methods used to obtain optically active allenes. Some stereochemical and synthetic aspects of chiral allenes are summarized in references 2 and 3; there the literature has been reviewed up to December 1971. Since then a wealth of stereochemical data has appeared. In order to present a consistent and almost complete summary of the stereochemistry of allenes, the already reviewed stereochemical results are reconsidered in the context of the material now available.

Dynamical aspects (reactions of chiral allenes) are treated partly in connection with the chemical methods for the deduction of absolute configurations of chiral allenes. Additionally, a discussion of some special reactions completes this chapter on (static and dynamic) stereochemistry of allenes.

6.1. Absolute configuration and optical purity

6.1.1. Structure and nomenclature of chiral allenes

Chirality is a property that differentiates an object from its mirror image and therefore is related to the concept of symmetry. Objects related to each other as image and mirror image are called enantiomers.[1] Clearly, any object can have only one enantiomer.

Symmetry may be defined mathematically in terms of a geometrical "symmetry group" G of several "symmetry operations". A chiral object cannot be superimposed onto its mirror image by rotation (and/or translation). Therefore, an object is achiral if only the position in space is altered on reflection or rotation–reflection, i.e. it is achiral if its symmetry group contains planes of reflection and/or improper rotations.

Chirality of molecules may be described on several levels. The first level uses the model of spatially rigid molecules, which allows the systematic treatment of chirality for idealized objects on the basis of the geometrical arrangements of points in space. It starts from the conceptional dissection of allenes into the achiral skeleton of symmetry D_{2d} with four ligand sites to which the substituents are attached (Fig. 1). The ligands may be atoms or groups of atoms. The allenic skeleton is polycentric and of the symmetry of an irregular tetrahedron, and thus it may be related geometrically to the monocentric methane skeleton of symmetry T_d of the regular tetrahedron.

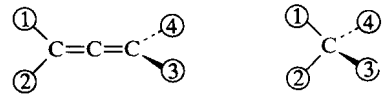


Figure 1

If the achiral ligands of the molecules are represented by points of a definite quality, symmetry operations on the rigid skeleton are identical with interchanges of the ligands, i.e. permutations of the ligands among the sites. Such permutations give in general a different isomer, but there are some permutations whose effect is the same as simply rotating the molecule and/or replacing it by its mirror image. The truly different isomers produced in this way are termed "permutation isomers".

On this level of describing stereoisomers a particular molecule is characterized by a spatial arrangement of indexed points (the ligands) on the ligand sites, and molecules with exclusively identical ligands have the symmetry of the molecular skeleton. A systematic treatment of the possibilities for getting chiral allenes through arrangements of different or like ligands on the four allenic sites may be achieved by "partition diagrams",[3] where like ligands are arranged in horizontal boxes (Fig. 2).

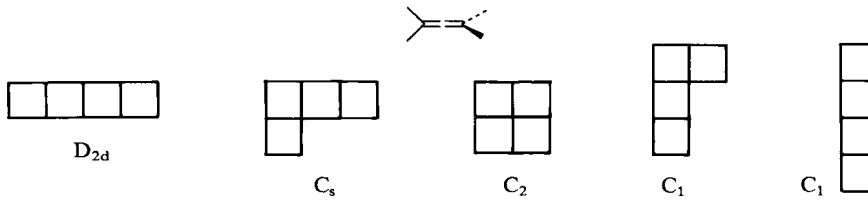


Figure 2

Accordingly, allenes where the chirality is due to the spatial arrangement of achiral ligands may have two identical ligands. Generally, chiral allenes are of the types **a**–**c** in Fig. 3. Methane derivatives must have four different ligands to become chiral. The type of chirality associated with an appropriate arrangement of ligands around the polycentric allenic skeleton is usually referred to as "axial chirality", whereas monocentric systems give rise to "centrochirality" ("asymmetric atoms").[1]

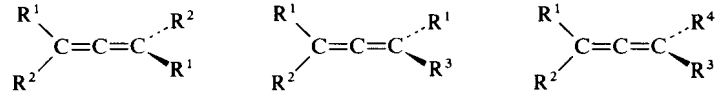
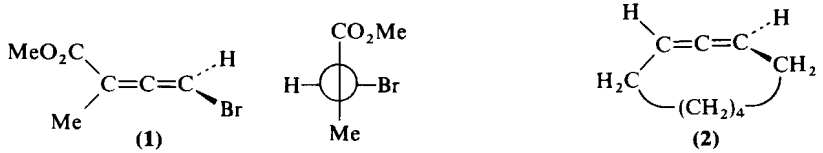


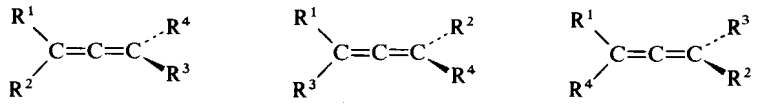
Figure 3

The configurational nomenclature of enantiomeric allenes is related to their axial chirality by the Cahn–Ingold–Prelog convention.[1c] For the purpose of nomenclature the enantiomer **1** should be viewed along the allenic axis of the molecule and represented in an appropriate projection. According to the sequence rules for axially chiral molecules, front groups have precedence over rear groups. This gives the precedence order CO_2Me > Me > Br > H for **1**, and consequently the enantiomer **1** has the (*S*) configuration. Similarly, the configurational nomenclature for chiral cyclic allenes, such as (*R*)-cyclonona-1,2-diene (**2**), is established.



So far, concerning the general treatment of isomeric allenes, we have restricted ourselves to enantiomers, which are related to each other simply by interchange of geminal substituents. Permutation of ligands among arbitrary ligand sites may give constitutional isomers (structural isomers), which may or may not be chiral. Permutations of the ligands in allenes of types **a** and **b** to give non-enantiomeric isomers only lead to achiral constitutional isomers of symmetry C_{2v} ($R^2 = R^3$) or C_s ($R^2 \neq R^3$), respectively, with like geminal ligands. On the other hand, from allenes of type **c**, with four different ligands, three non-enantiomeric chiral isomers may be generated, e.g. the ensemble **d** in Fig. 4.

On the geometrical level of point-models for molecules, stereoisomeric allenes therefore are described by the terms "constitution" and "configuration", i.e. the sequential arrangements of atoms in the molecules regardless of their directions in space (constitution) and the relative positions of atoms

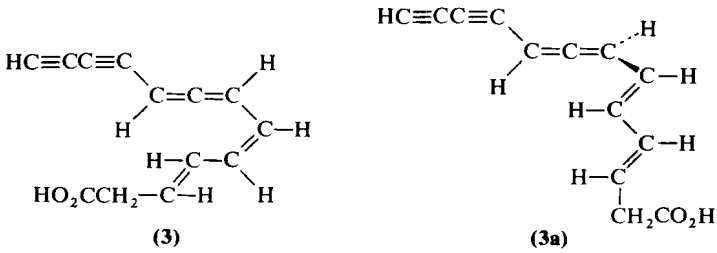


(d)

Figure 4

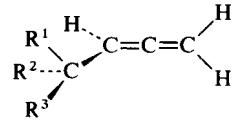
and/or groups in space (configuration). Thus stereoisomeric allenes may be classified as enantiomers and diastereomers. Enantiomers can be differentiated by their chiral (pseudoscalar) properties, whereas diastereomers (constitutional isomers) may be differentiated by their scalar molecular properties.

The next level of describing stereoisomers takes into consideration the actual disposition of the atoms in space in terms of bond distances, bond angles, dihedral angles, etc. (conformation). Mycomycin (**3**), $[\alpha]_D$ −130° (EtOH), is a naturally occurring allene[2b,4] which may have *cis* and *trans* double bonds in the ligand. In the arbitrary absolute configuration **3a** it is one of eight possible stereoisomers.Consequently, one may distinguish configurational diastereomers (of the type **d** in Fig. 4) and conformational diastereomers (like those of mycomycin, **3**).



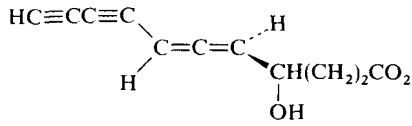
(3) (3a)

Enantiomerism in allenes may, of course, arise also from the presence of one or more asymmetric atoms in the molecules, i.e. chirality may be induced by a chiral ligand of the otherwise achiral allenic radical, such as in **e** where one hydrogen is substituted by a centrochiral substituent. For such cases the configurational nomenclature refers to the rules for asymmetric atoms.[1c]

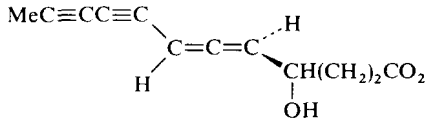


(e)

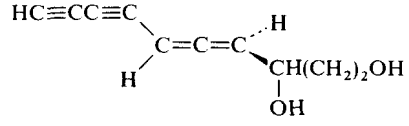
More interesting is the combination of the allenic axial chirality and the atomic centrochirality of a ligand. Some naturally occurring diyne-allenes



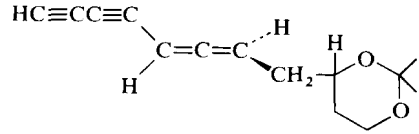
(4) $[\alpha]_D$ +380° (EtOH)



(5) $[\alpha]_D$ +360° (EtOH)

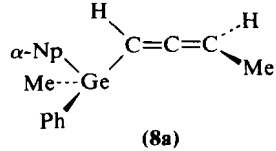


(6) $[\alpha]_D$ +210° (EtOH)

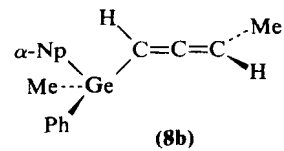


(7) $[\alpha]_D$ +210° (EtOH)

(**4**–**7**) show this type of chirality.[5–7] Concerning the allenic axial chirality, the dextrorotatory molecules have the (*S*) configuration. For such kinds of molecules the structural criterion for enantiomerism in each subunit, namely interchange of geminal ligands, applied to only one chiral subunit gives rise to diastereomers, which may be differentiated by their scalar properties. For instance, the diastereomers **8a** and **8b**, arbitrarily given as the (*S*)(*R*) and (*S*)(*S*) isomers, exhibit measurably different ^{1}H n.m.r. for their diastereotopic allenic hydrogen atoms and the protons of the methyl groups.[8]

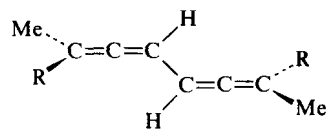


(8a)



(8b)

For allenes of the type **4**–**8** there exist four optically active isomers. If two chiral allenic subunits are combined to form a diallene there are fewer than four optically active isomers, since the *meso* isomer with a centre of symmetry will be achiral. For instance, the chemical syntheses of the acyclic diallenes **9** and **10** afforded only *meso* forms.[9] On the other hand,



(9) R = Ph
(10) R = Bu^t