Tetrahedron Letters xxx (2013) xxx–xxx

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Theoretical modelling of the epoxidation of vinylallenes to give cyclopentenones

Gérard Audran, Paul Brémond, Sylvain R. A. Marque, Anouk Gaudel-Siri, Didier Siri *, Maurice Santelli *

Université d'Aix-Marseille & CNRS, Institut de Chimie Radicalaire—UMR 7273, Avenue Escadrille Normandie-Niemen, 13397 Marseille Cedex 20, France

ARTICLE INFO

Article history:
Received 12 July 2013
Revised 18 September 2013
Accepted 23 September 2013
Available online xxxx

Dedicated to the memory of Professor A. Guillemonat (1909–1999) who introduced allene chemistry at the University of Aix-Marseille

Keywords:
Epoxidation
Vinylallene
Vinylallene epoxide
Cyclopentenone
Electrocyclization

ABSTRACT

Epoxidation of vinylallenes (1,2,4-pentatrienes) can lead to cyclopent-2-enones. Various experimental results suggest that these reactions are concerted and that vinylallene oxides undergo a concerted and thermal ring-closing reaction to give cyclopentenones. In 1977, this view has been supported by the epoxidation of a non-racemic 4-methyl-2,3,5-hexatriene to give a non-racemic 2,5-dimethyl-2-cyclopenten-1-one. Indeed, for the cyclization of (3*E*)-4-methyl-2,3-epoxy-2,3,5-hexatriene or (4*E*)-4-methyl-3,4-epoxy-2,3,5-hexatriene into 2,5-dimethyl-2-cyclopenten-1-one, a transition structure for the concerted rearrangement was located, and IRC calculations showed it linked together. The activation barrier predicted at the B3LYP/6-311++G(3df,3pd)//B3LYP/6-31G(d) level of theory is 80.9 or 124.2 kJ mol^{-1}, respectively and the reaction is exothermic by 127.2 or 89.2 kJ mol^{-1}, respectively.

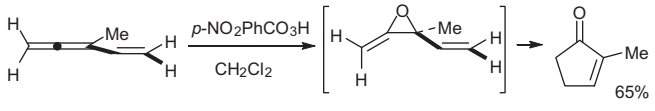
© 2013 Published by Elsevier Ltd.

1. Introduction

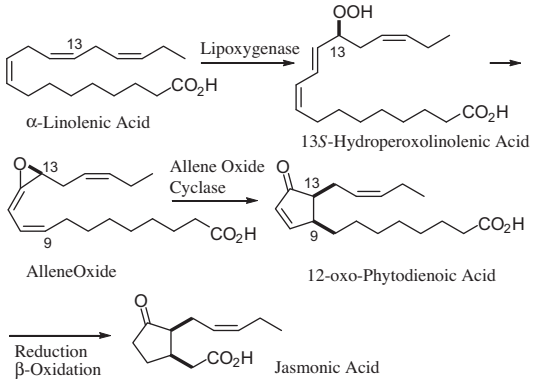
In 1969, Grimaldi and Bertrand discovered that the epoxidation of vinylallenes, alkylated on the allene chain, afforded exclusively, or preponderantly, conjugated cyclopentenones (Scheme 1).[1]

This cyclization has thus gained importance since it was shown that biologically important cyclopentenones arise from the isomerization of vinylallene oxides coming from the dehydration of hydroperoxides of dienic fatty acids.[2] The allene oxide synthases are enzymes of two structurally-unrelated types. In plants, a subfamily of cytochrome P450, designated as *CYP74A*, uses the hydroperoxides of linoleic and linolenic acids as substrates. Both these 9- and 13-hydroperoxides may be converted to allene oxides and subsequently give rise to plant signalling molecules (Scheme 2).[3] In corals, one of the functions of a catalase-related hemoprotein is the allene oxide synthase activity. *Plexaura homomalla* is renowned for its high content of prostaglandin esters, which contribute up to 2–3% of the coral dry weight. These marine invertebrates, as well as starfish, form allene oxides from the 8*R*-hydroperoxide of arachidonic acid. This enzyme may be involved in the biosynthesis of the cyclopentenone eicosanoids such as the clavulones.[4]

In this Letter, we attempt to provide a better understanding of this interesting cyclization reaction by the report of calculated structures.[5–7]



Scheme 1. Epoxidation of 3-methyl-1,2,4-pentatriene.



Scheme 2. Biosynthesis in plants of jasmonic acid from α-linoleic acid.

* Corresponding authors. Tel.: +33 491289181; fax: +33 491288545.
E-mail addresses: didier.siri@univ-amu.fr, m.santelli@univ-amu.fr (M. Santelli).

0040-4039/$ - see front matter © 2013 Published by Elsevier Ltd.
http://dx.doi.org/10.1016/j.tetlet.2013.09.110

2. Results

The chemistry of allene oxides is well documented, and a valence tautomeric triad allene oxide, cyclopropanone and oxyallyl has been investigated (Scheme 3).[8,9] For allene bearing bulky substituents, peracid epoxidation can lead to isolable allene oxides.[10–12]

First we focused on the structure of alkyl substituted allene epoxides. Calculated thermodynamic data at the B3LYP/6.311++G(3df,3pd) level of theory showed that the (*Z*)-isomers were slightly more stable than the (*E*)-ones (Scheme 4).

From epoxidation of vinylallenes, various cyclopentenones have been synthesized. Remarkably, the cyclization occurred by using several oxidizing reagents, as peracids,[1,13] Payne reagent,[14] mercuric and thallic acetates,[15] photoepoxidation,[16] *t*BuOOH/VO(acac)$_2$ (Sharpless reagent)[17] and dimethyl-dioxirane.[18]

The mechanism of the formation of cyclopentenones by epoxidation of vinylallenes is particularly puzzling.[8,19] In a seminal work, it was demonstrated that the epoxidation of enantiomerically enriched vinylallene (−)-(*R*)-4-methyl-2,3,5-hexatriene (**1**) led to non-racemic (−)-(*S*)-2,5-dimethyl-2-cyclopenten-1-one (**3**) as the unique product.[20] It was reasonable to assume that the epoxidation of **1** could lead to four transient allene oxides **2a**–**d** (Scheme 5 and Table 1). The epoxidation on the vinyl group led to stable allene-epoxide.[1] While the obtention of (−)-(*S*)-**3** from allene oxides (*S*)-**2a** or (*S*)-**2c** appeared to be possible, it was not the same for the two others and particularly the (*Z*)-isomer **2b** (previous theoretical calculations concerning the isomerization of vinyl allene oxides into cyclopentenones dealt only with the (*E*)-isomers).

A gas electron diffraction method[21] and an ab initio study[22] of vinylallene (1,2,4-pentatriene) conformations indicated that an anti conformer (*s*-trans conformation) must dominate in the gas phase, however, the preference was less for the vinylallene than for either 1,3-butadiene or 1,3-pentadiene. Concerning 1,3-dimethyl-1,2,4-pentadiene **1**, computational studies at the B3LYP/6-311++G(3df,3dp) level of theory revealed that the *s*-trans conformation was more stable than the *s*-cis one by only 6.0 kJ mol^{-1}.[23]

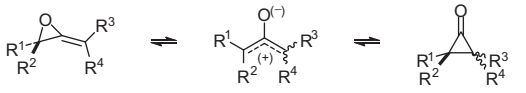
Table 1
Relative energies of various isomers of (*R*)-4-methyl-2,3,5-hexatriene epoxides (B3LYP/6-311++G(3df,3pd) level of theory)

Allene oxide	ΔE (au)	$\delta\Delta E$ (kJ mol^{-1})	ΔG (au)	$\delta\Delta G$ (kJ mol^{-1})
2a	−348.035 407	0.00	−347.918 131	0.00
2b	−348.034 563	2.22	−347.917 044	2.84
2c	−348.027 614	20.44	−347.911 571	17.22
2d	−348.025 833	25.12	−347.909 710	22.07

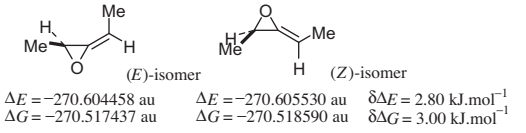
It is well known that epoxidation of α-, β- or γ-allenic alcohols give rise to cyclic keto-ethers or lactones resulting from a nucleophilic attack at the allene oxide intermediates by the hydroxy group (Scheme 6).[24]

But, in the course of oxidation of hydroxylated vinylallenes by Sharpless reagent, Cha could not find any product resulting from a similar intramolecular nucleophilic attack by the α- or β-hydroxy group in the crude reaction mixture.[17c] Moreover, the annulations proceeded stereoselectively (Scheme 7).

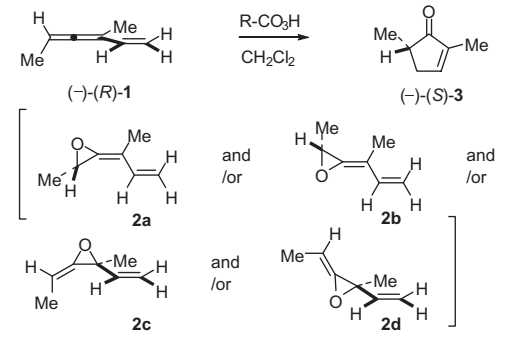
Consequently, one can consider that the discrete vinylallene oxide does not actually exist and that the epoxidation of the *s*-cis conformer of the vinylallene gives rise in two steps directly to the cyclopentenone (Scheme 8). All published results concerning the cyclopentenones formation by epoxidation of vinylallenes bear on vinylallenes which can exist as *s*-cis conformers.



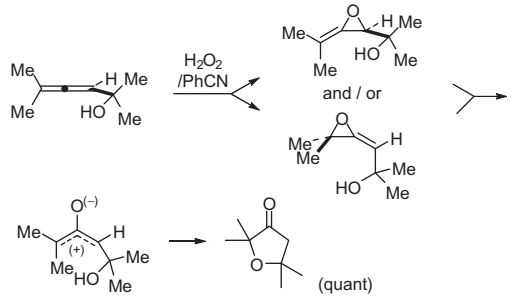
Scheme 3. Valence isomerization of allene oxides.



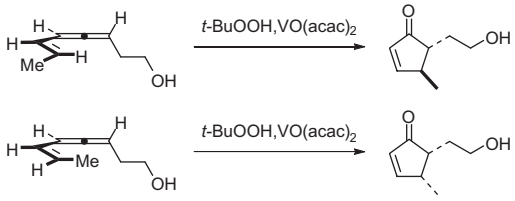
Scheme 4. Relative stability of (*E*)- and (*Z*)-2,3-pentadiene oxides.



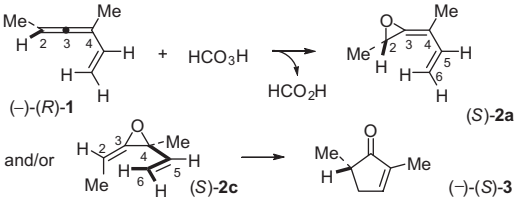
Scheme 5. Epoxidation of (*R*)-4-methyl-2,3,5-hexatriene **1**.



Scheme 6. Epoxidation of 2,5-dimethyl-3,4-hexadien-2-ol.



Scheme 7. Epoxidation of *cis*- and *trans*-3,4,6-octatrien-1-ols.



Scheme 8. Hypothetical mechanism for the epoxidation of **1**.

Download English Version:

https://daneshyari.com/en/article/5262956

Download Persian Version:

https://daneshyari.com/article/5262956

Daneshyari.com