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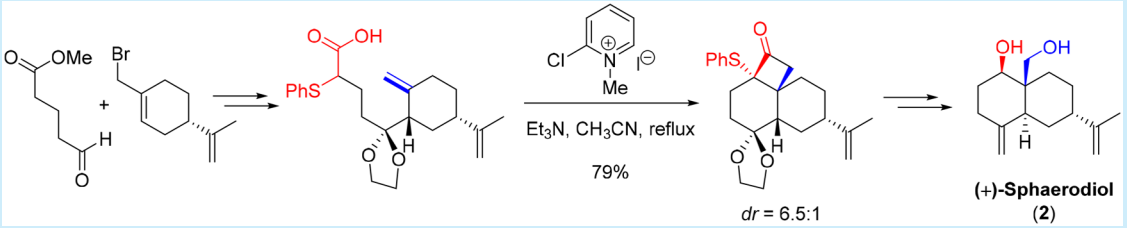
Intramolecular [2 + 2] Cycloadditions of Alkyl(phenylthio)ketenes: Total Synthesis of (+)-Sphaerodiol

Xiang Wu,*[,†] Hai-Jun Wang,[†] Yong-Shuang Huang,[†] and Wei-Dong Z. Li*[,‡]

[†]Anhui Province Key Laboratory of Advanced Catalytic Materials and Reaction Engineering, School of Chemistry and Chemical Engineering, Hefei University of Technology, Hefei 230009, China

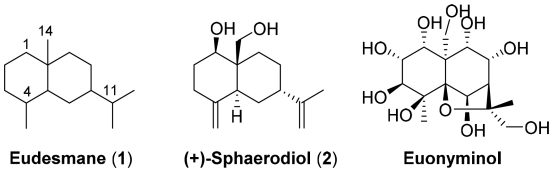
[‡]School of Life Science and Engineering, Southwest Jiaotong University, Chengdu 610031, China

Supporting Information



ABSTRACT: Asymmetric total synthesis of (+)-sphaerodiol (**2**) has been achieved. A key step is an intramolecular [2 + 2] cycloaddition of alkyl(phenylthio)ketene for rapid assembly of the decalin ring.

The Asteraceae family contains over 1000 eudesmanes, with almost every conceivable oxidation pattern within the carbon framework.[1] Considerable efforts have been devoted to the total synthesis of eudesmane sesquiterpenoids over the past decades,[2] in which the rigid decalin skeleton **1** possessing multiple hydroxyl functions (i.e., euonyminol) posed a significant synthetic challenge. It is thus highly desirable to develop a facile and diversified strategy for the total synthesis of eudesmane sesquiterpenes.

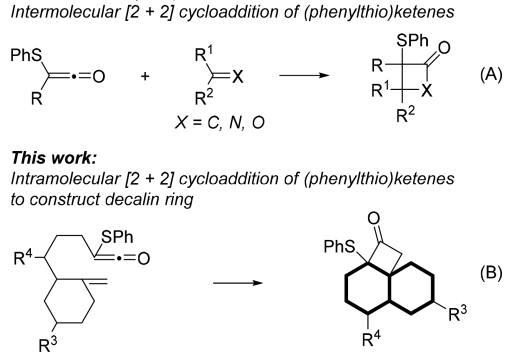


Eudesmane (**1**) (+)-Sphaerodiol (**2**) Euonyminol

The natural eudesmane sesquiterpene compound (+)-sphaerodiol (**2**)[3] with C1, C14-dihydroxyl was isolated from *polyachyrus sphaerocephalus* by Bohlmann and co-workers in 1991.[4] In continuation of our ongoing studies on the total synthesis of bioactive sesquiterpenoids,[5] we report herein the development of a novel method of intramolecular [2 + 2] cycloaddition of alkyl(phenylthio)ketene to construct the decalin ring (Scheme 1B) and its application in the total synthesis of (+)-sphaerodiol (**2**).

The cycloaddition of ketenes to alkenes is a generally popular method for the synthesis of cyclobutanone derivatives.[6] Although the intramolecular [2 + 2] cycloadditions of ketenes to alkenes generate synthetically useful polycyclic compounds with a high degree of regio- and stereocontrol,[7] this method has been applied by a few groups for the synthesis of natural products.[8] Heterosubstituted ketenes, such as the alkyl(phenylthio)ketenes, have shown enhanced reactivity toward functional groups (Scheme 1A).[9] To the best of our knowledge, the intramolecular cycloaddition of those type of ketenes has not been explored systematically. Therefore, it is in our interest to explore the intramolecular [2 + 2] cycloaddition of alkyl(phenylthio)ketene for the construction of the decalin ring system of typical eudesmanes (Scheme 1B).

Scheme 1. [2 + 2] Cycloaddition of (Phenylthio)ketenes



Previous studies by Ghosez and co-workers[10] have shown that the ketenes prepared by the treatment of acid chloride **3a** and **3e** (entries 1 and 5, Table 1) with Et_3N provided the cycloadducts **4a**, **e** in only 3% yield both.[11] When the phenylthio group was introduced to the α position of carbonyl acid chloride **3b**, the yield of the cycloadduct **4b** was only slightly increased to 6% (entry 2, Table 1). Therefore, we set out to investigate other substrates for the cycloaddition.

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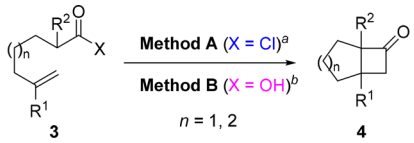
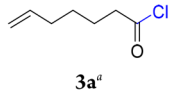
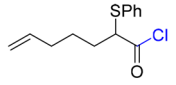
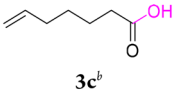
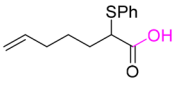
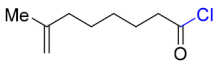
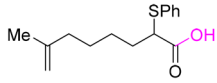
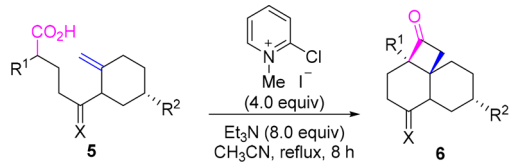
Table 1. Intramolecular Ketene [2 + 2] Cycloaddition of 3

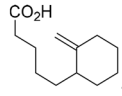
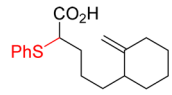
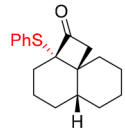
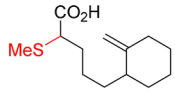
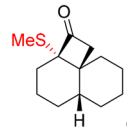
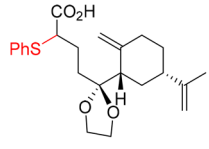
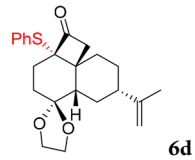
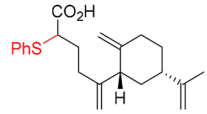
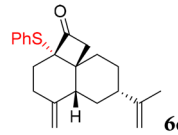
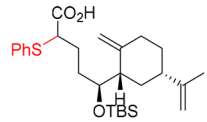
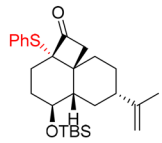


entry	structure of **3**	cycloadduct **4**	yield[c]
1	 **3a**[a]	 **4a**	3%
2	 **3b**[a]	 **4b**	6%
3	 **3c**[b]	 **4a**	0%
4	 **3d**[b]	 **4b**	70%
5	 **3e**[a]	 **4e**	3%
6	 **3f**[b]	 **4f**	62%

[a]**Method A**: Ketenes were generated by adding the solution of Et_3N to the solution of acid chloride in refluxing CH_2Cl_2. [b]**Method B**: Ketenes were generated by adding the solution of carboxylic acid to a solution of Et_3N and 2-chloro-*N*-methylpyridinium iodide in refluxing CH_3CN. [c]Isolated yield.

Table 2. Intramolecular Ketene [2 + 2] Cycloaddition of 5



entry	structure of **5**	cycloadduct **6**	yield[a] (*dr*)[b]
1	 **5a**	*Recovered* **5**	
2	 **5b**	 **6b**	70% (2.5:1)[b]
3	 **5c**	 **6c**	57% (2.5:1)[b]
4	 **5d**	 **6d**	79% (6.5:1)[c]
5	 **5e**	 **6e**	89% (1.6:1)[c]
6	 **5f**	 **6f**	17% (>20:1)[c]

[a]Isolated yield. [b]Determined by ^1H NMR. [c]Determined by separation through chromatography.

It has been reported that activation of carboxylic acid with Mukaiyama's reagent is superior to the corresponding acid chloride for the in situ generation of ketene and subsequent cyclization.[8f] Mukaiyama's reagent (2-chloro-*N*-methylpyridinium iodide)[12] is an effective reagent to generate ketenes *in situ* for subsequent [2 + 2] cycloadditions with alkenes,[13] allenes,[14] aldehydes,[15] imines,[16] and hydrazones.[17] Although initial studies on the acid **3c** with Mukaiyama's reagent failed to yield desired intramolecular cycloadduct **4a**, when the phenylthio-substituted acid **3d** and **3f** were added to a solution of Mukaiyama's reagent and Et_3N in refluxing CH_3CN, cycloadducts **4b** and **4f** were obtained as single diastereomers in 70% and 62% yields, respectively (entries 4 and 6, Table 1). Based on these results, it could be inferred that the introduction of phenylthio-substituent to ketene can enhance the reactivity and the phenylthio-substituted ketene could be generated efficiently by the reaction of acid with Mukaiyama's reagent.

Then, in order to construct the decalin ring of eudesmane, some elaborated substrates were employed. The cycloaddition was carried out under the optimal conditions as described above. Results are summarized in Table 2. The α-phenylthio acid **5b**, which has a four-carbon-atom tether conformationally restricted by a six-membered ring, was investigated to give the tricyclic cycloadduct **6b** in 70% yield with 2.5:1 dr.[18] For comparison, the acid **5a** without a phenythio-substituent could not afford any cycloadduct. Moreover, the methylthio-substituted acid **5c** (entry 3) could also produce tricyclic adduct **6c** with the same diastereoselectivity but in a lower yield of 57%. As illustrated in entries 1−3, the reactivity of phenylthio-substituted ketene is superior to that of methylthio-substituted ketene, probably because the phenyl group works as an inductively withdrawing group when bonding with the sulfur atom which could stabilize the ketene more effectively and avoid the side reactions.[8i] Further modified substrates **5d** and **5e** can also be converted to the cycloadducts in excellent yields (entries 4 and 5); however, **5f** gave the corresponding product **6f** with excellent diastereoselectivity albeit in a low yield (entry 6).[19]

As an example, the α-phenylthio acid **5d** as the key intermediate to the synthesis of (+)-sphaerodiol (**2**) was prepared as follows (Scheme 2). (*S*)-Perillyl bromide **7**, obtained from commercially available (*S*)-perillyl aldehyde,[20] reacted with the aldehyde **8** to give the alcohol **9** via a Barbier-type reaction.[21] Alcohol **9** was a diastereomeric mixture that

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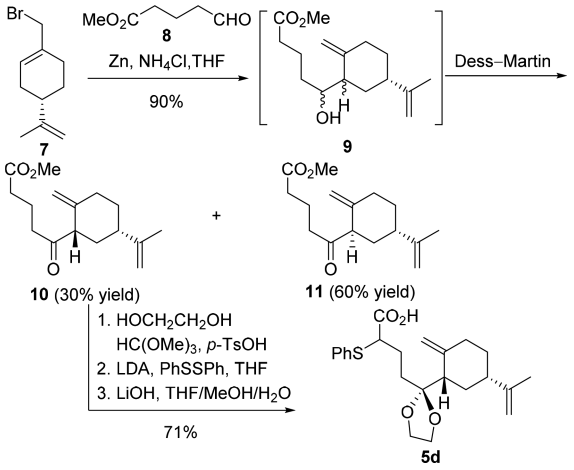
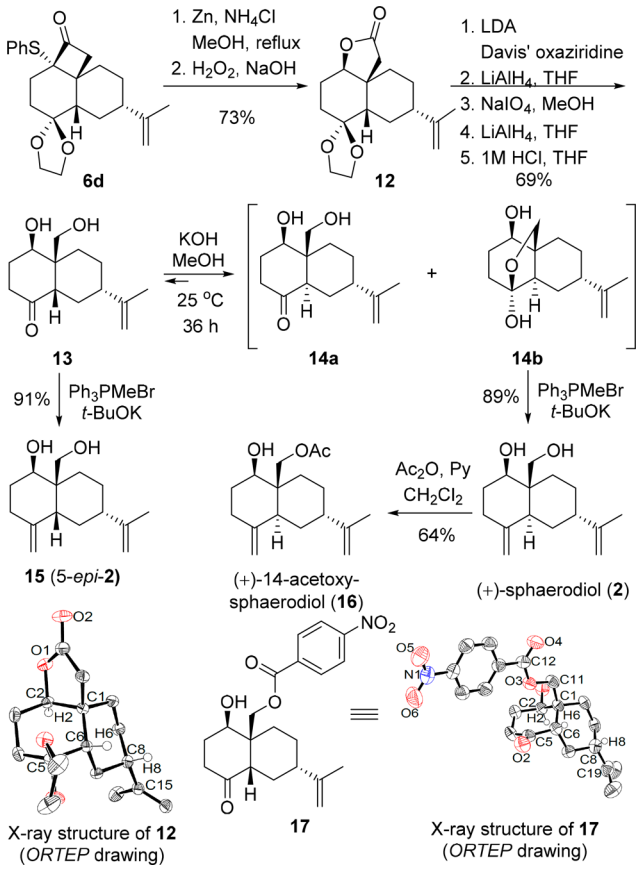
Scheme 2. Synthesis of Acid 5d



was converted to ketones **10** and **11** by Dess-Martin oxidation.[22] Compound **10** was then separated by column chromatography. Protection of the ketone in **10** and introduction of phenylthio group, followed by hydrolysis of ester, provided acid **5d** in 71% yield.

The cycloadduct **6d** derived from acid **5d** underwent smooth desulfurization upon exposure to activated Zn dust and NH_4Cl in MeOH under reflux, and was then oxidized by H_2O_2, which gave five-membered lactone **12** in 73% yield over two steps (Scheme 3). The structure of **12** was confirmed by single crystal X-ray analysis (see Supporting Information (SI)). A hydroxyl group was introduced to the α position of lactone **12** by the reaction of enolate with Davis' oxaziridine.[23] Then the compound was reduced with $LiAlH_4$ to give diastereomeric lactols. Without separation, the resultant lactols underwent oxidative cleavage using $NaIO_4$ to furnish a formate aldehyde. The formate aldehyde residue was further reduced with $LiAlH_4$ to give C1, C14-diol. Deprotection of the ketal group using 1 M HCl afforded **13** in 69% yield over five steps. The *cis*-fused decalin ring system of **13** was confirmed according to the X-ray crystallographic analysis of a single crystal of ester derivative **17** (see SI). Ketone **13** could be epimerized under basic conditions to give a mixture of **13** and *trans*-**14**(**a, b**) in a ratio of 4:1. Thus, by a repeated epimerization−separation sequence, undesired ketone **13** was mostly converted to a mixture of ketone **14a** and hemiketal **14b**. Wittig reaction of **13** with Ph_3PMeBr and *t*-BuOK gave compound **15** (5-*epi*-**2**), and Wittig reaction of **14** furnished target compound **2**. 14-Acetoxy-lα-hydroxy-5,10-bis-*epi*-eudesma-4(15),11(13)-diene (**16**) was obtained after acylation of the 14-hydroxy of compound **2**. The synthetic product **2** (^{1}H NMR, ^{13}C NMR, IR and HRMS)[24] and **16** (^{1}H NMR, IR) were identical spectroscopically to the natural products as previously reported.[25]

Scheme 3. Total Synthesis of (+)-Sphaerodiol (2)



In summary, we have described the intramolecuar [2 + 2] cycloaddition of alkyl(phenylthio)ketene prepared from the corresponding acids to construct a decalin ring, and demonstrated the utility of the strategy for the first asymmetric total synthesis of (+)-sphaerodiol (**2**) in 6% yield via 15 steps.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b00407.

Experimental procedures, X-ray structures of **12** and **17**, and spectral data (PDF)

Accession Codes

CCDC 1588362 and 1588364 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: wuxiang@hfut.edu.cn.
*E-mail: wdli@cqu.edu.cn.

ORCID

Xiang Wu: 0000-0001-5428-9063

Notes

The authors declare no competing financial interest.

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(3) The compound was isolated from *polyachyrus sphaerocephalus*. Its systematic name is 1,14-dihydroxy-5,10-bisepieudesma-4(15),11 (13)-diene, yet we refer to the compound as sphaerodiol for convenience. The absolute configuration of sphaerodiol has not been confirmed, and we report here the first asymmetric synthesis of (+)-sphaerodiol.

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