

## Highly Stereoselective Synthesis of (*E, E*)-3,7-Dimethyl-2,6-decadiene-1, 10-diol

Zuo Sheng LIU<sup>1</sup>, Jiong LAN<sup>1</sup>, Li Zeng PENG<sup>1</sup>, Yu Lin LI<sup>1\*</sup>, Ya Cheng XING<sup>2</sup>, Wen CEN<sup>2</sup>

<sup>1</sup> National Laboratory of Applied Organic Chemistry and Institute of Organic Chemistry,  
Lanzhou University, Lanzhou 730000

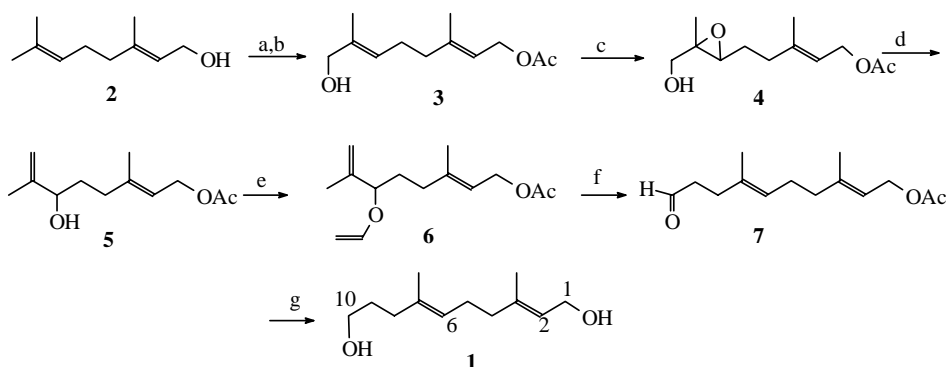
<sup>2</sup> Department of Chemistry, Qingdao University, Qingdao 266071

**Abstract:** A total synthesis of (*E, E*)-3,7-dimethyl-2,6-decadiene-1,10-diol, using 1,3-transformation of 2, 3-epoxy alcohol and Claisen rearrangement of allyl vinyl ether as key steps, is described.

**Keywords:** 2,3-Epoxy alcohol, 1,3-transformation: Claisen rearrangement, synthesis.

The diol **1**<sup>1</sup>, a queen butterfly pheromone was isolated from queen butterfly (*Danaus gillippus belenice*). Syntheses of this compound were reported from the orthoester Claisen rearrangement<sup>2</sup>, the rearrangement of allyl siloxyvinyl ether<sup>3</sup> and the anionic [2,3]-sigmatropic rearrangement of allylic sulfide<sup>4</sup>. In light of their biological interest, it seemed desirable to design a more efficient route to this substance. Thus, we wish to report a short, stereoselective synthesis of **1** utilizing the 1, 3-transformation of 2, 3-epoxy alcohol and the Claisen rearrangement of allyl vinyl ethers. (**Scheme1**)

**Scheme 1**



Reagents and conditions: a) Ac<sub>2</sub>O, pyridine, rt, 2 h, 100%; b) SeO<sub>2</sub>, *t*-BuOOH, CH<sub>2</sub>Cl<sub>2</sub>, rt, 2 h, 64%; c) VO (acac)<sub>2</sub>, *t*-BuOOH, C<sub>6</sub>H<sub>6</sub>, reflux, 2 h, 90%; d) Ph<sub>3</sub>P, I<sub>2</sub>, pyridine,

Et<sub>2</sub>O/CH<sub>3</sub>CN (5/3), 0°C, 1 h, then added 1*eq* H<sub>2</sub>O, 38°C, 6 h, 94%; e) Hg (OAc)<sub>2</sub>, ethyl vinyl ether, reflux, 24 h, 83%; f) sealed tube, 110°C, 1 h, 90%; g) LiAlH<sub>4</sub>, Et<sub>2</sub>O, rt, 12 h, 96%.

Treatment of geraniol **2** with Ac<sub>2</sub>O in pyridine gave geranyl acetate in 100% yield. SeO<sub>2</sub> oxidation of the terminal double bond of geranyl acetate produces the alcohol **3** in 64% yield<sup>5</sup>. Treatment of the alcohol **3** with VO(acac)<sub>2</sub> and *t*-BuOOH under reflux for 2 h gave the 2,3-epoxy alcohol **4** in 90% yield<sup>6</sup>. By our method<sup>7</sup>, allylic alcohol **5** was obtained in 94% yield with Ph<sub>3</sub>P, pyridine, I<sub>2</sub> and H<sub>2</sub>O.

By treatment with a large excess of ethyl vinyl ether containing freshly recrystallized mercuric acetate<sup>8</sup>, the allylic alcohol **5** was converted into the corresponding allyl vinyl ether **6**. The allyl vinyl ether **6** was pyrolysed in sealed tube at 110 °C under Ar for 1 h to obtain the aldehyde **7** in 90% yield<sup>9</sup>. The *trans:cis* isomer ratio which was determined by GC, was 93:7. Treatment of the aldehyde function group and cleavage of the acetate provides the pheromone **1** in 96% yield. The spectroscopic properties of this material are fully consistent with its assigned structure<sup>10</sup>.

### Acknowledgment

This work was financially supported by the National Natural Science Foundation of China (Grant No. 29672015)

### References and Notes

1. J. Meinwald, Y. C. Menwald, and P. H. Mazzocchi, *Science*, **1969**, *164*, 1174.
2. D. H. Miles, D. Loew, W. S. Johnson, A. F. Kluge, and J. Meinwald, *Tetrahedron Lett.*, **1978**, (30), 3019.
3. J. A. Katzenellenbogen, and K. J. Christy, *J. Org. Chem.*, **1974**, *39* (23), 3315.
4. Y. Masaki, K. Sakuma, and K. Kaji, *Chem. Pharm. Bull.*, **1985**, *33* (5), 1930.
5. M. Unbriet, and K. B. Sharpless, *J. Am. Chem. Soc.*, **1977**, *99*, 5526.
6. K. B. Sharpless, and R. C. Michaelson, *J. Am. Chem. Soc.* **1973**, *95*, 6136.
7. Z. S. Liu, J. Lan, and Y. L. Li, *Tetrahedron: Asymmetry*, **1998**, *9* (21), 3755.
8. A. W. Burgstahlen, I. C. Nordin, *J. Am. Chem. Soc.*, **1961**, *83*, 198.
9. D. J. Faulker, and M. R. Petersen, *Tetrahedron Lett.*, **1969**, (38), 3243.
10. spectral data:  
Compound **1**: IR: 3328, 2933, 2871, 1668, 1057, 1006, 920 cm<sup>-1</sup>. EIMS (*m/z*): 199 (0.05%, M+1), 183 (0.15, M-15), 180 (0.2, M-18), 167 (1), 149 (1), 121 (6), 95 (100Z), 85 (33), 67 (97), 55 (58), 43 (30), 41 (93). <sup>1</sup>HNMR (400MHz, CDCl<sub>3</sub>): δ (ppm) 5.39 (t, J=6.4Hz, 1H, CH=), 5.15(d, J=6.4Hz, 1H, CH=), 4.13 (d, J=6.4Hz, 2H, CH<sub>2</sub>O), 3.61 (t, J=6.4Hz, 2H, CH<sub>2</sub>O), 2.54 (brs, 2H, 2OH), 2.18-2.12 (m, 2H, CH<sub>2</sub>), 2.09-2.04 (m, 2H, CH<sub>2</sub>), 1.70-1.63 (m, 4H, 2CH<sub>2</sub>), 1.65 (s, 3H, CH<sub>3</sub>), 1.62 (s, 3H, CH<sub>3</sub>).

Received 29 December 1998