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# APPLICATION OF THE RUTHENIUM-CATALYZED OXIDATIVE CLEAVAGE OF OLEFINS TO THE ALDEHIDES IN THE SYNTHEIS OF (S)-14-METHYL-1-OCTADECENE, THE SEX PHEROMONE OF *Lyonetia clerkella*

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**ABSTRACT.** The synthesis of (14S)-methyl-octadec-1-ene, the sex pheromone of peach leafminer moth *Lyonetia clerkella* is described using a new protocol for the oxidative cleavage of the olefin **4**.

***Key words: Oxidative cleavage / Ruthenium catalyst / Pheromone***

## INTRODUCTION

The peach leafminer, *Lyonetia clerkella* (Linaeus), is distributed in Japan, South Korea, Taiwan, China, India, Europe, and Madagascar. Infestation by this insect causes almost complete defoliation of the trees and reduces cropping and fruit production potential for the future, which typically affects to fruit trees such as apple, pear, cherry, plum, quince and peach.

Sugie *et al.* identified the sex pheromone of the moth as 14-methyl-1-octadecene **1**[1]. To establish the absolute configuration of the natural pheromone, Kato and Mori developed two synthetic routes to the enantiomers of **1** starting from the enantiomers of methyl-β-hydroxyisobutyrate[2] and from (R)-citronellic acid[3]. Biological tests with these synthesized compounds showed that the natural pheromone is (S)-14-methyl-1-octadecene, and that there is no antagonistic activity of the (R)-enatiomer.

## RESULTS AND DISCUSSIONS

During the last years, various strategies have been developed for the synthesis of **1**[4-7]. In this paper we described a new protocol for the synthesis of (14S)-methyl-1-octadecene **1** starting from (R)-citronellic acid (Scheme 1). Our procedure is based on the known literature method[3], and the key step was the oxidative cleavage of olefin **4** to aldehyde **5**.

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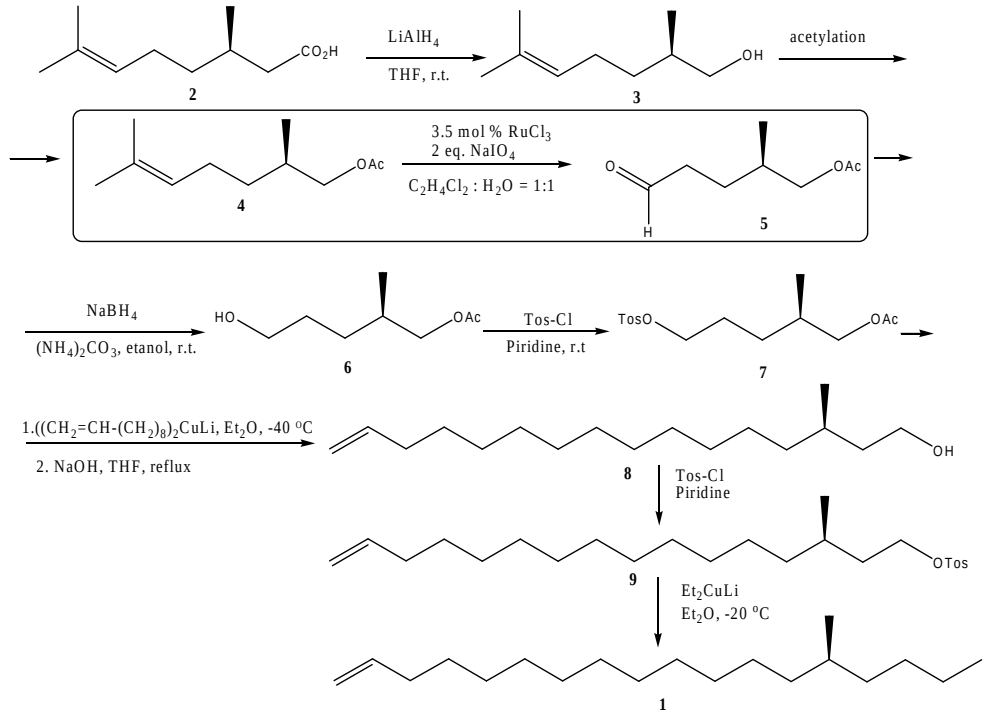


***Scheme 1***

To obtain aldehyde **5** from the olefin **4**, K. Mori *et al.* have used the ozonization of the olefin followed by a reductive workup[3] (ozone was bubbled through the stirred and cooled mixture at -70 ºC), the compound **5** being obtained in 60 % yield. For the sake of safety and convenience, a great deal of efforts have been directed at developing alternative methods to cleave olefins to aldehydes, especially in a catalytic manner. D. Yang and C. Zhang have developed three ruthenium-based catalytic oxidation methods for the cleavage of a wide range of olefins to aldehydes[8]. The oxidative cleavage of olefin **4** to aldehyde **5** involved the use of ruthenium trichloride as catalyst (3.5 mol %), sodium periodate as terminal oxidant and two immiscible liquid phases, *i. e.*, 1,2-dichloroethane and water, as the solvent system. The yield of **5** was 53 % after purification by column chromatography. This new protocol represents a very useful alternative for the ozonolysis of olefins followed by a reductive workup, since $RuCl_3$ is easy to handle, is not expensive and the reaction proceeded under mild conditions at room temperature.

Having the key derivative **7** in hand, the next step was the synthesis of **8** by treatment of **7** with di(9-decenyl)-cuprate and the resulting product was submitted to alkaline hydrolysis to give **8** in 60 % yield. The second-elongation was made by treatment of the tosylate **9** with lithium diethylcuprate yielding (S)-**1**.

## CONCLUSIONS

In summary, we prepared (14S)-methyloctadec-1-ene **1**, the overall yield for the all steps being 28%. All the data recorded for our synthetic sample of **1** matched those reported in the literature[3].

## EXPERIMENTAL SECTION

$^1$H-NMR (500 MHz) spectra were recorded at *rt* in $C_6D_6$ on a Bruker 500 MHz spectrometer, using the solvent line as reference. Electron impact (70 eV) mass spectra were obtained on Hewlett-Packard MD 5972 GC-MS instrument. GC analyses were performed on a Hewlett-Packard HP 5890 gas chromatograph. A HP-5MS capillary column (30 m x 0.25 mm x 0.33 µm) and helium gas were used for separations.

**General procedure for the oxidative cleavage of 4:**

To a stirred mixture of olefin **4** (5 mmol, 1.0 g) and $RuCl_3$ (0.175 mmol, 3.5 mol%, 36.3 mg) in 1,2-dichloroethane (25 ml) and distilled water (25 ml) was added in portions $NaIO_4$ (10 mmol, 2.14 g) over a period of 5 min. at room temperature. The color turned from black to yellow immediately. The reaction was monitored by TLC. After completion in 8 h, the reaction mixture was quenched with saturated aqueous solution of $Na_2S_2O_3$, and the two layers were separated. The aqueous layer was extracted with EtOAc three times. The combined organic layer was washed with water and brine, respectively, dried over anh. $MgSO_4$, filtered, and concentrated. The residue was purified by column chromatography (EtOAc : *n*-hexane = 2 :3) to give the desired aldehyde **5** as a colorless oil (0.5 g, 53%). $^1$H NMR (500 MHz, $C_6D_6$, δ ppm ): 0.68 (d, 3 H, J = 6.5 Hz, 3-C*H*$_3$), 1.08-1.47 (m, 7 H), 1.81 (s, 3 H, -COC*H*$_3$), 4.01-4.10 (m, 2 H, -C*H*$_2$-O-), 9.38 (s, 1 H, C*H*O); $^{13}$C NMR (125 MHz, $C_6D_6$, δ ppm): 18.79, 20.34, 28.50, 29.26, 35.20, 41.09, 62.24, 169.94, 200.37; GC: $R_t$ = 19.56 min; MS: *m/z* 129 (2 %) $[M - COCH_3]^+$, 43 (100 %) $[COCH_3]^+$.

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