

SYNTHESIS OF THE ACETATE OF (+)-2,6-DIMETHYLHEPTA-1,5-DIEN-3-OL -  
THE RACEMIC FORM OF THE SEX PHEROMONE OF *Pseudococcus comstocki*

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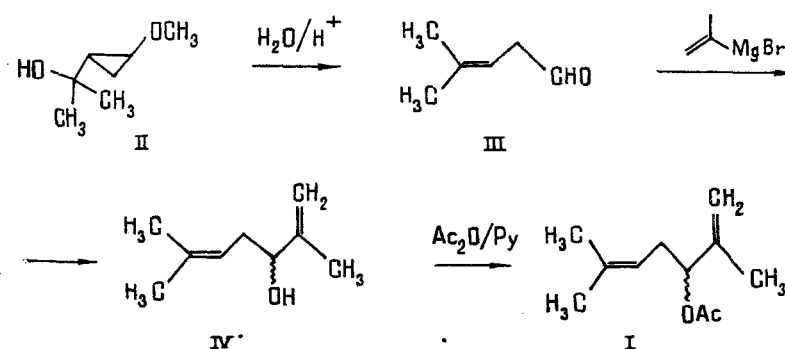
UDC 547.512

4-Methylpent-3-enal has been synthesized by the dehydration of trans-2-(1-hydroxy-1-methylethyl)-1-methoxycyclopropane, and this has been brought into reaction with propen-2-ylmagnesium bromide. Acetylation of the carbinol so formed gave the acetate of (+)-2,6-dimethylhepta-1,5-diene-3-ol - the racemic form of the sex pheromone of the Comstock mealybug.

The acetate of (+)-2,6-dimethylhepta-1,5-dien-3-ol possesses a high attraction action for males of *Pseudococcus comstocki* (Comstock mealybug) [1]. In its attractive capacity it is close to the natural pheromone - the acetate of (+)-2,6-dimethylhepta-1,5-dien-3-ol [2].

(+)-2,6-Dimethylhepta-1,5-dien-3-ol has been obtained previously by several methods: by the epoxidation of 2,6-dimethylhepta-1,5-diene followed by reduction of the monoepoxide with aluminum isopropanolate [2], by the photochemical oxidation of 2,6-dimethylhepta-1,5-diene in the presence of tetrabutylammonium tetrahydroborate [3], by the rearrangement of 2,6-dimethyl-1-phenylsulfinylhepta-2,5-diene [4], and also by the reaction of isopentenyllithium and methacrolein [5].

The approach proposed in the present paper to the synthesis of the acetate of (+)-2,6-dimethylhepta-1,5-dien-3-ol (I) is based on the use as key compound of trans-2-(1-hydroxy-1-methylethyl)-1-methoxycyclopropane (II), a method of obtaining which from readily available starting materials we have described in [6]. The cyclopropylcarbinyl homoallyl isomerization of carbinol (II) gave 4-methylpent-3-enal (III) [7], which was caused to react with propen-2-ylmagnesium bromide. The yield of (+)-2,6-dimethylhepta-1,5-dien-3-ol (IV) in this reaction was 70%. Subsequent acetylation of the alcoholic group led to the desired product with a yield of 30%, calculated on the initial carbinol (II).



The structures of the (+)-2,6-dimethylhepta-1,5-dien-3-ol (IV) and its acetate (I) were confirmed by the correspondence of their physicochemical constants to those given in the literature, and also by their PMR spectra.

#### EXPERIMENTAL

PMR spectra were taken on a Tesla BS-467A spectrometer with a working frequency of 60 MHz using carbon tetrachloride as solvent; chemical shifts are given in the scale relative to the signal of TMS (internal standard).

Scientific-Research Institute of Physicochemical Problems, V. I. Lenin Belorussian University, Minsk. Translated from *Khimiya Prirodnikh Soedinenii*, No. 5, pp. 747-748, September-October, 1988. Original article submitted December 4, 1987.

4-Methylpent-3-enal (III) was synthesized from 10 g of trans-2-(1-hydroxy-1-methylethyl)-1-methoxycyclopropane (II) and 50 ml of 0.25 N sulfuric acid by the procedure described in [7]. This gave 4.1 g of 4-methylpent-3-enal (III) (53), bp 62-64°C (70 mm Hg),  $n_D^{18}$  1.4469. According to the literature: bp 128°C (760 mm Hg);  $n_D^{18}$  1.4486 [7].

(±)-2,6-Dimethylhepta-1,5-dien-3-ol (IV). At 0-5°, 5 g of 4-methylpent-3-enal (III) in 25 ml of tetrahydrofuran was added to a solution of prop-1-en-2-ylmagnesium bromide in 75 ml of absolute tetrahydrofuran obtained from 1.8 g of magnesium and 9 g of 2-bromopropene. The reaction mixture was stirred at room temperature for 1 h, and 50 ml of a saturated aqueous solution of ammonium chloride was added. The solvent was driven off in a rotary evaporator, the organic layer was separated off, and the aqueous layer was extracted with ether (4 × 30 ml). The combined ethereal extract was washed with saturated sodium bicarbonate solution. After the solvent had been eliminated, vacuum distillation gave 5.0 g (70%) of (+)-2,6-dimethylhepta-1,5-dien-3-ol (IV) (70%), bp 83-84°C (15 mm Hg),  $n_D^{17}$  1.4640. According to the literature: bp 70-71°C (13 mm Hg),  $n_D^{15}$  1.4647 [5]. PMR spectrum ( $\delta$ , ppm): 1.6 s (3H, CH<sub>3</sub>), 1.67 s (8H, 2CH<sub>3</sub>, CH<sub>2</sub>), 1.9-2.3 m (2H, CH, OH): 3.8 t (1H, CH, J = 6 Hz), 3.8 t (1H, CH, J = 6 Hz), 4.5-5.4 m (3H, 3CH).

The acetate of (+)-2,6-dimethylhepta-1,5-dien-3-ol (I) was obtained from (+)-2,6-dimethylhepta-1,5-dien-3-ol (IV) and acetic anhydride in pyridine [5]. Yield 80%, bp 55-56°C (3 mm Hg),  $n_D^{17}$  1.4481. According to the literature: bp 68-70°C (15 mm Hg),  $n_D^{25}$  1.4400 [5]. PMR spectrum ( $\delta$ , ppm): 1.6 s (3H, CH<sub>3</sub>), 1.7 s (8H, 2CH<sub>3</sub>, CH<sub>2</sub>), 1.9 s (3H, CH<sub>3</sub>), 2.27 t (1H, CH, J = 6 Hz), 4.7-5.6 m (3H, 3CH).

#### SUMMARY

The acetate of (+)-2,6-dimethylhepta-1,5-dien-3-ol - the racemic form of the sex pheromone of the Comstock mealybug - has been obtained in three stages from trans-2-(1-hydroxy-1-methylethyl)-1-methoxycyclopropane with an overall yield of 30%.

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