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SYNTHESIS OF THE RACEMIC SEX PHEROMONE OF Pseudococcus comstocki

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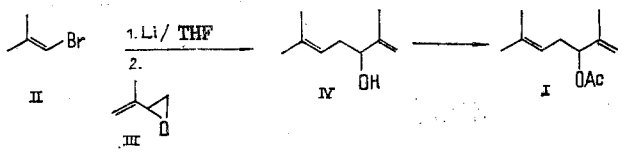
The synthesis of the acetate of 2,6-dimethylhepta-1,5-dien-3-ol – the sex pheromone of the Comstock bug – has been carried out by condensing isobutenyllithium with 3,4-epoxy-2-methylbut-1-ene and acetylating the 2,6-dimethylhepta-1,5-dien-3-ol formed. The overall yield of pheromone was 46%.

(+)-3-Acetoxy-2,6-dimethylhepta-1,5-diene (I) has been identified as the sex pheromone of the Comstock bug Pseudococcus comstocki (Kuwana) [1, 2]. At the present time it has been adopted in the USSR for wide use in the practice of the quarantining and protection of plants [3].

Synthesis of (+)-(I) are known that are based on the oxidation of 2,6-dimethylhepta-2,5-diene [2, 4], the condensation of methacrolein with prenyllithium [5] and of 4-methylpent-4-enal with isopropylmagnesium bromide [6], and an eight-stage transformation of 2,5-dimethylpyridine [7]. In the present paper we discuss the synthesis of the racemic acetate (I) by the condensation of the Li derivative of isobutenyl bromide (II) with 3,4-epoxy-2-methylbut-1-ene (III).

It is known that monohydroxy-1,3-dienes interact with organocuprates and with organomagnesium and organolithium compounds in the majority of cases nonstereoselectively with the formation of products of formal 1,4- and 1,2-addition [8-13]. The latter predominates on the use of vinyllithium reagents in THF [10]. In actual fact, on the interaction of the isobutenyllithium obtained from the bromide with the oxide (III) in THF the required alcohol (IV) was formed regioselectively. Its acetylation led to the desired acetate (I) with an overall yield of 46%, calculated on (II). The physicochemical characteristics (boiling point n_D, and IR and PMR spectra of the alcohol (IV) and acetate (I)) that had been synthesized corresponded to the characteristics published for these compounds [5].



The acetate (I) obtained, which, according to GLC, had a purity of 96% exhibited a high attractant activity in the field with respect to males of the Comstock bug.

EXPERIMENTAL

IR spectra of solutions in CCl_4 were taken on a UR-20 instrument. PMR spectra were measured relative to TMS on a Tesla BS-467A spectrometer (60 Hz) in CCl_4, and GLC was

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conducted on a Chrom-5 instrument with a 3 × 25 mm column containing 5% of SE-30 on Chromaton NAW-DMCS.

2,6-Dimethylhepta-1,5-dien-3-ol (IV). Over 5 min, 3.3 g (39 mmole) of the epoxide (III) [15] was added at 0-5°C to a vigorously stirred solution of isobutenyllithium prepared from 5.3 g (39 mmole) of the bromide (II) [14] and 0.54 g (77 mg-atom) of Li in 50 ml of THF. The reaction mixture was stirred at 25°C for 8 h and was then filtered, the filtrate was neutralized with H_2SO_4 and was extracted with ether. The extract was washed with saturated NaCl solution, dried with $MgSO_4$, and evaporated in vacuum, and the residue was chromatographed on SiO_2. Elution with hexane–ether (10:1) gave 3.3 g (60%) of the alcohol (IV), bp 72-75°C (15 mm), n_D^{20} 1.4650. IR spectra (ν, cm^{-1}): 990, 1040, 1370, 1440, 2280, 2980, 3080, 3420. PMR spectrum (δ, ppm): 1.63 s (3 H, CH_3); 1.78 s (6 H, CH_3); 2.3 t (2 H, $CH_2C{\equiv}C$, J = 7 Hz); 4.1 t (1 H, CHO, J = 7 Hz); 4.7-5.5 m (3 H, HC≡C).

2,6-Dimethylhepta-1,5-dien-3-yl Acetate (I). Over 5 min, 0.7 g (8.9 mmole) of AcCl was added at 0°C to a stirred solution of 0.45 g (3.2 mmole) of the alcohol (IV) and 0.71 g (9 mmole) of pyridine in 10 ml of ether. The mixture was kept at 25°C for 3 h and, after the usual working up, 0.45 g (77%) of the acetate (I) was obtained with bp 70-72°C (16 mm). n_D^{20} 1.4447. IR spectrum (ν, cm^{-1}): 990, 1040, 1370, 1440, 1740, 2880, 3080, 3100. PMR spectrum (δ, ppm): 1.63 c (3H, CH_3); 1.73 s (6H, CH_3); 2.05 s (CH_3CO); 2.35 t (2H, $CH_2C{=}C$, J = 7 Hz); 4.7-5.5 m (4H, CHO, HC≡C).

SUMMARY

A simple synthesis of the Comstock bug pheromone from isoprene monoxide has been effected.

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