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(S)-(+)-Dihydromyrcene in the Directed Synthesis of Insect Pheromones

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Abstract

Via the selective oxidative transformations of double bonds in (+)-(3S)-3,7-dimethylocta-1,6-diene (dihydromyrcene), the main thermolysis product of (+)-cis-pinane, efficient schemes are developed for the synthesis of a number of optically active insect pheromones.

Key words: (S)-(+)–dihydromyrcene, pheromones, oxidation, ozonolysis

The thermolysis product of (+)-cis-pinane ¹ contains a mixture of isomeric hydrocarbons ² : ³ : ⁴ : ¹ at an approximateratio 55 : 7 : 10 : 28 (Scheme 1), among those the most important isomer is presented by (+)-(3S)-3,7-dimethylocta-1,6-diene (dihydromyrcene) ² used in the synthesis of exo and endo insect hormones [1]. The extraction of pure diene ² from the mixture of isomers by means of distillation is a laborious procedure. We proposed an alternative pathway based on the selective oxidative transformations of double bonds. It was established that dihydromyrcene ² could be subjected to the selective transformation in a mixture of compounds ¹–⁴ by means of partial ozonolysis of a thermolytic product of (+)-cis-pinane ¹, which leads to the cleavage of a trisubstituted double bond in diene (Scheme 2). The further reduction of the peroxide prod-

Reagents and conditions: a. H₂/Ni. b. 510–550 °C.

Scheme 1.
Products of ozonolysis using NaBH₄ results in the formation of alcohol 5, whereas the use of Me₂S as a reducer leads to the formation of aldehyde 6. In some cases, in order to obtain target chiral block-synths from diene 2 one needs to perform the terminal double bond cleavage with conserving the isopropenyl fragment. The selective protection of the trisubstituted double bond in this fragment can be provided owing to the oxidation thereof into epoxide 7. Compounds 5–7 can be readily isolated with the purity level of 94–97% from the isomeric mixture of hydrocarbons by means of fractional distillation under reduced pressure.

The further ozonolytic cleavage of the terminal double bond in compound 7 and the removal of epoxy protection in the resulting ester 8 via the action of AI₂₃ leads to the formation of ester 9. Replacing the AI₂₃ by MgI₂ results in the formation of ketoester 10.

Alcohol 5 served a synthon in the synthesis of the pheromones of Chinese bean weevil.
(2E,7S)-3,7-dimethylocta-2-endoic acid 11 and African monarch butterfly (2E,7S)-3,7-dimethylocta-2-ene-1,8-diol 12 (Scheme 3) [2].

Basing on compounds 6 and 9 we have developed synthetic schemes for the pheromones of ants belonging to genera Crematogaster Myrmica (6R)-6-methyloctane-3-one 13 (2S)-2,6-dimethylheptyl-5-ene-1-ol 14 and corresponding aldehyde 15 (Scheme 4) [3].

Aldehyde 6 was also used in the synthesis of (R)-(–)-methyltridecane-2-one 19 (Scheme 5), that represents a sex pheromone of a strawworm such as aspen leaf beetle [4].

CONCLUSION

Thus, basing on the products of selective oxidative transformations of (S)-(+) -dihydromyrcene we have developed efficient pathways for the synthesis of a number of optically active insect pheromones.

REFERENCES