SYNTHESIS OF cis-UNDEC-5-en-2-one – THE PHEROMONE OF THE PEDAL GLANDS OF Damaliscus dorcas dorcas

B. G. Kovalev, A. M. Sorochinskaya, and L. A. Avdeeva

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The ketone cis-undec-5-en-2-one (III) has been isolated as the main volatile component of the pedal glands of the bontebok Damaliscus dorcas dorcas [1]. Several syntheses of this compound are known: by the conjugate addition of B-(hept-1-ynyl)-9-borobicyclo[3.3.1]nonane to methyl vinyl ketone [2], by the alkylation of pent-4-yn-1-ol [3], and via dihydrojasmone [4]. All these syntheses are complicated, with many stages.

We have performed a two-stage synthesis of the ketone (III) by the reaction of levulinic aldehyde (I) with n-hexyltriphenylphosphonium bromide (II) under the conditions described by Bestmann et al. [5].

$$\underset{\text{I}}{CH_3CO(CH_2)_2CHO} \xrightarrow[[Me_3Si]_2NNa]{\underset{\text{II}}{n\text{-}C_6H_{13}PPh_3\cdot Br},\ THF} \underset{\text{III}}{CH_3CO(CH_2)_3CH{=}CHC_5H_{11}}.$$

Levulinic aldehyde is readily obtained by the oxidation of acetopropyl alcohol with pyridinium chlorochromate in methylene chloride with a yield of 81%, bp 88-92°C (2 mm), n_D^{20} 1.4258.

The reaction of the aldehyde (I) with the phosphonium salt (II) gave the ketone (III) with a yield of 65%, bp 106°C (10 mm), n_D^{20} 1.4462. The isomeric purity of (III) was 97% of the cis isomer.

Thus, we have developed a new two-stage synthesis of cis-undec-5-en-2-one from the industrially available acetopropyl alcohol with an overall yield of 52%.

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