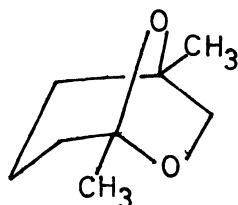
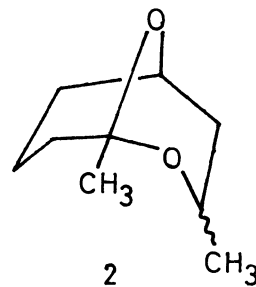


## CONVENIENT SYNTHETIC ROUTE TO (+) -FRONTALIN

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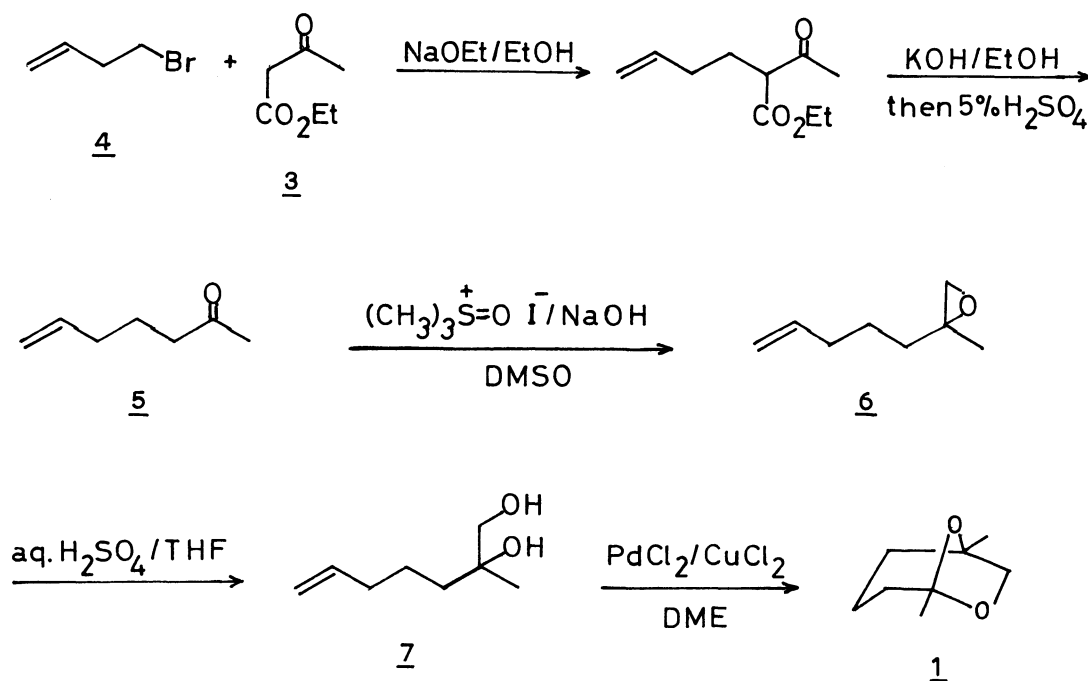
(±)-Frontalin was synthesized in a few steps sequence starting from ethyl acetoacetate involving intramolecular cyclization using palladium chloride as catalyst.

Frontalin, a pheromone of southern pine beetle, *Dendroctonus frontalis*, was first isolated by Kinzer,<sup>1)</sup> in 1969, and the structure was determined as 1,5-dimethyl-6,8-dioxabicyclo [3.2.1] octane (1) by spectroscopic data and confirmed by a synthesis of its racemate.<sup>1,2)</sup> On account of its structural novelty and economic value, this compound has been studied extensively.<sup>3-5)</sup> By now, several syntheses (racemic as well as asymmetric) have reported for frontalin.<sup>6-11)</sup>

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In the course of our studies on the palladium catalysed cyclisation, we recently reported a three-step synthesis of 1,3-dimethyl-2,9-dioxabicyclo [3.3.1] nonane (2), an insect attractant.<sup>12)</sup> As an extension of this reaction, here, we wish to report a convenient synthetic method for the synthesis of (+)-frontalin starting from commercially available ethyl acetoacetate.

Alkylation of ethyl acetoacetate (3) with 4-bromo-1-butene (4) (NaOEt-EtOH, reflux, 12 h), followed by alkaline hydrolysis and decarboxylation (aq. KOH, then 5% H<sub>2</sub>SO<sub>4</sub>, reflux, 1 h) gave 6-hepten-2-one (5) in 71% yield. Ketone 5 was treated with oxysulfurane [(CH<sub>3</sub>)<sub>3</sub>S=O I<sup>-</sup>/NaH] in dry dimethyl sulfoxide at 60 °C for 1 h gave epoxide 6 in 55% yield. Acid hydrolysis of epoxide (5% H<sub>2</sub>SO<sub>4</sub>, THF) gave the diol 7 which was cyclised directly to (+)-frontalin (1) (50% yield) using palladium chloride as catalyst in anhydrous dimethoxyethane with copper (II) chloride as reoxidant for palladium. The spectral properties (IR, <sup>1</sup>H and <sup>13</sup>C NMR, MS) of the product were identical with those reported for 1.<sup>1,6,9,13)</sup>



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