Category

Synthesis of Natural Products and Potential Drugs

Key words

(±)-hirsutene

triquinanes

Ireland-Claisen rearrangement

radical cyclization



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Tandem Radical Approach to Linear Condensed Cyclopentanoids. Total Synthesis of (±)-Hirsutene J. Am. Chem. Soc. 1985, 107, 1448–1449.

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Radical-Initiated Polyolefinic Cyclizations in Linear Triquinane Synthesis. Model Studies and Total Synthesis of (±)-Hirsutene *Tetrahedron* **1985**, *41*, 3943–3958.

Synthesis of (±)-Hirsutene

Significance: Hirsutene is a linear triquinane that was isolated from the fungi *Coriolus consors* in 1976. Its lack of heteroatomic functional groups along with the presence of four contiguous stereocenters and two quaternary carbon atoms render this condensed cyclopentanoid natural product challenging. In 1985, Curran and Rakiewicz reported an elegant synthesis of (±)-hirsutene employing a late-stage radical cyclization.

Comment: Accessed in two steps from the corresponding enone, acetate **A** was converted into lactone **B** by Ireland–Claisen rearrangement followed by phenylselenolactonization. Elimination, S_N2' reaction, and deprotection furnished carboxylic acid **E**. Further transformation led to iodoenyne **H**, which underwent *5-exo-*trig/*5-exo-*dig radical cyclization cascade in the presence of AIBN/Bu₃SnH to afford (±)-hirsutene.