

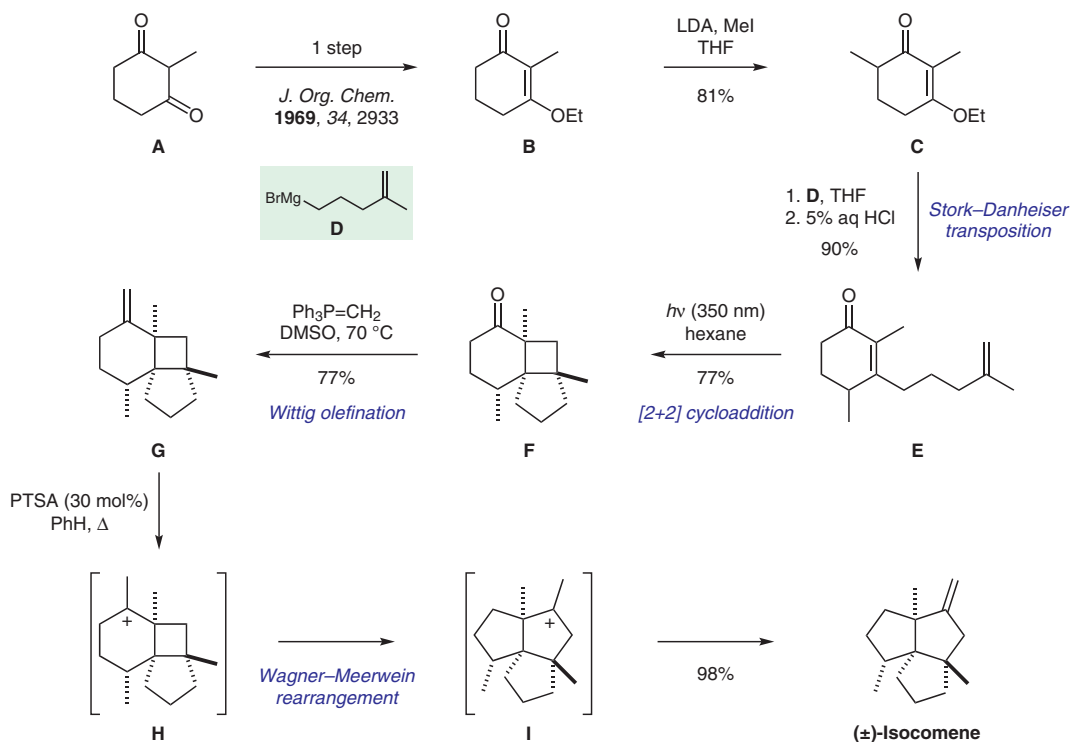
(±)-isocomene**Stork–Danheiser
transposition****[2+2]
photocycloaddition****Wittig olefination****Wagner–Meerwein
rearrangement**Synfact
Classic

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Total Synthesis of (±)-Isocomene

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Synthesis of (±)-Isocomene



Significance: Isolated from rayless goldenrod (*Isocoma wrightii*) in 1977, (±)-isocomene possesses an intriguing tricyclic carbon skeleton containing four adjacent stereocenters, three of which are quaternary. These structural features render the natural product a challenging target for synthesis. Pirrung was able to access isocomene in seven steps starting from commercially available 2-methylcyclohexa-1,3-dione. His strategy features an intramolecular [2+2] photocycloaddition to install three contiguous quaternary stereocenters and a Wagner–Meerwein rearrangement to furnish the tricyclic core.

Comment: Starting from commercially available 2-methylcyclohexa-1,3-dione **A**, cyclohexenone **E** was accessed using a Stork–Danheiser transposition. Irradiation of the enone effected intramolecular [2+2] photocycloaddition to furnish cyclobutane **F** containing three adjacent quaternary stereocenters. Treatment of intermediate **G** with acid effected a Wagner–Meerwein rearrangement to give (±)-isocomene in excellent yield.