

rearrangements

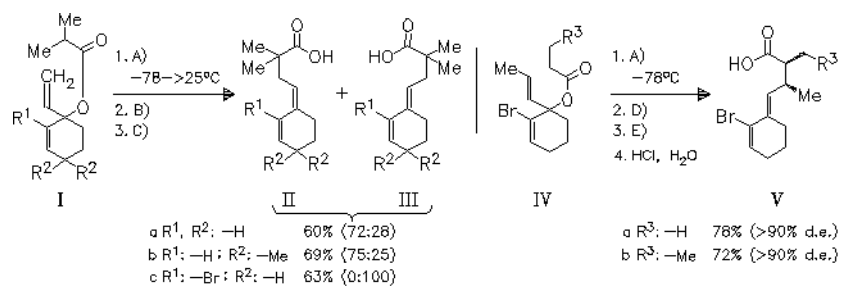
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Intramolecularly Competitive Ireland–Claisen Rearrangements: Scope and Potential Applications to Natural Product Synthesis. —

The Ireland–Claisen rearrangement of cyclic bis-allylic esters proceeds with complete regioselectivity via the exocyclic alkene. The stereochemical outcome depends on the substitution pattern of bis-allylic esters. Thus, 2-substituted cyclohexenyl esters lead to (E)-configured products, whereas starting from 6-substituted cyclohexenyl esters (Z) isomers are obtained. The relative stereochemistry of the pentenoic unit can be controlled by enolate geometry. —

(HONG, SANG-PHYO; LINDSAY, HARRIET A.; YARAMASU, TRIPURA; ZHANG, XIAOWEI; MCINTOSH, MATTHIAS C.; J. Org. Chem. 67 (2002) 7, 2042-2055; Dep. Chem. Biochem., Univ. Ark., Fayetteville, AR 72701, USA; EN)



A): TIPS-O-Tf, KN(TMS)₂, Et₂O
 B): K₂CO₃, THF/MeOH/H₂O, 25°C

C): HCl, NaCl, H₂O
 D): AcOH, H₂O, -78 → 25°C

E): Bu₄NF, THF, 0 → 25°C

