

The Takai–Oshima–Lombardo Methylenation of Carbonyl Compounds

Category

Metals in Synthesis

Key words

carbonyl compounds

methylenation

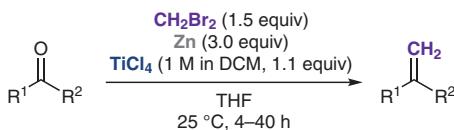
olefination

titanium

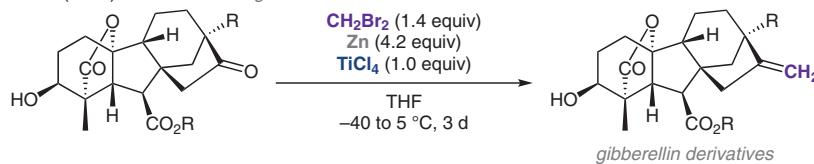
zinc

Synfact
 Classic 

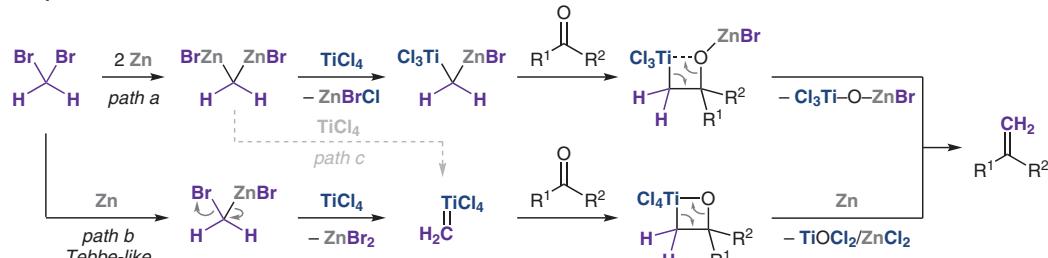
Takai, Oshima (1978):



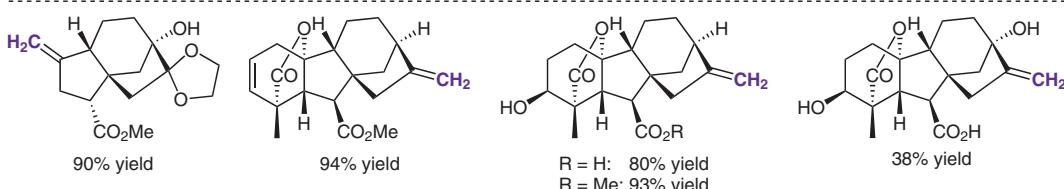
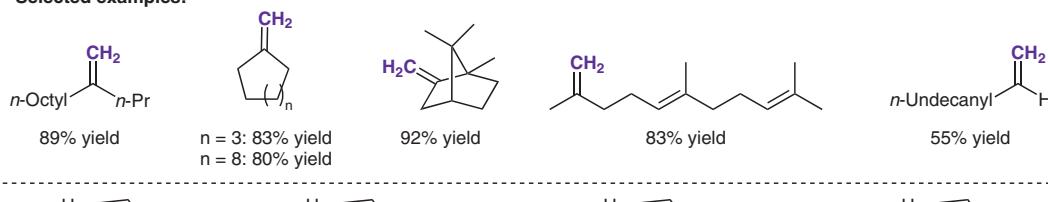
Lombardo (1982): Lombardo's reagent



— Proposed mechanism:



— Selected examples:



Significance: The Takai–Oshima–Lombardo methylenation is a synthetically important reaction to convert carbonyl compounds into alkenes. Initially introduced by Takai, Oshima and co-workers in 1978, this transformation was further elaborated by Lombardo in 1982. The Zn/ CH_2Br_2 /TiCl₄ system is also known as the Lombardo–Oshima reagent.

Comment: The highly electrophilic methylenation reagent is formed *in situ* and stable at low temperatures. In contrast to the Wittig reaction, this protocol is applicable to base-sensitive substrates, as demonstrated by the olefination of enolizable gibberellin derivatives without erosion of enantiomeric excess. The structure of the active species is assumed to be a *gem*-dimetallic species (see path a).