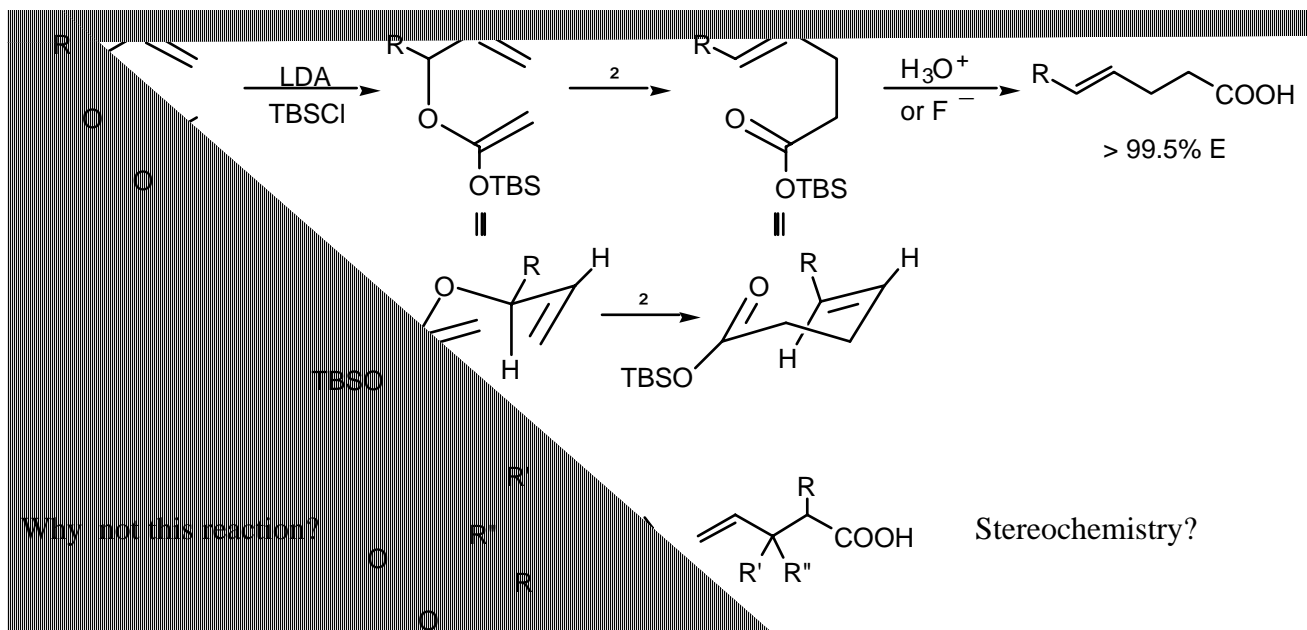
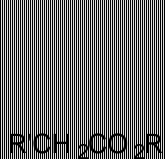


Ester Enolate Claisen Rearrangement

Ireland, R. E.; *et al. J. Am. Chem. Soc.* **1976**, *98*, 2868; **1972**, *94*, 5897; *J. Org. Chem.* **1981**, *46*, 479



Stereochemistry of formation of silyl ketene acetals

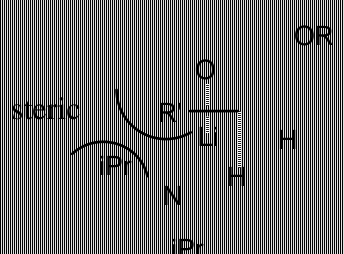
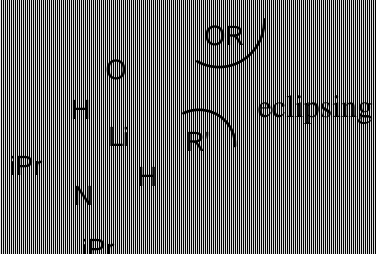


LDA
THF;
TBSCl

R' OR
H OTBS

LDA
THF
HMPA;
TBSCl

R' OTBS
H OR

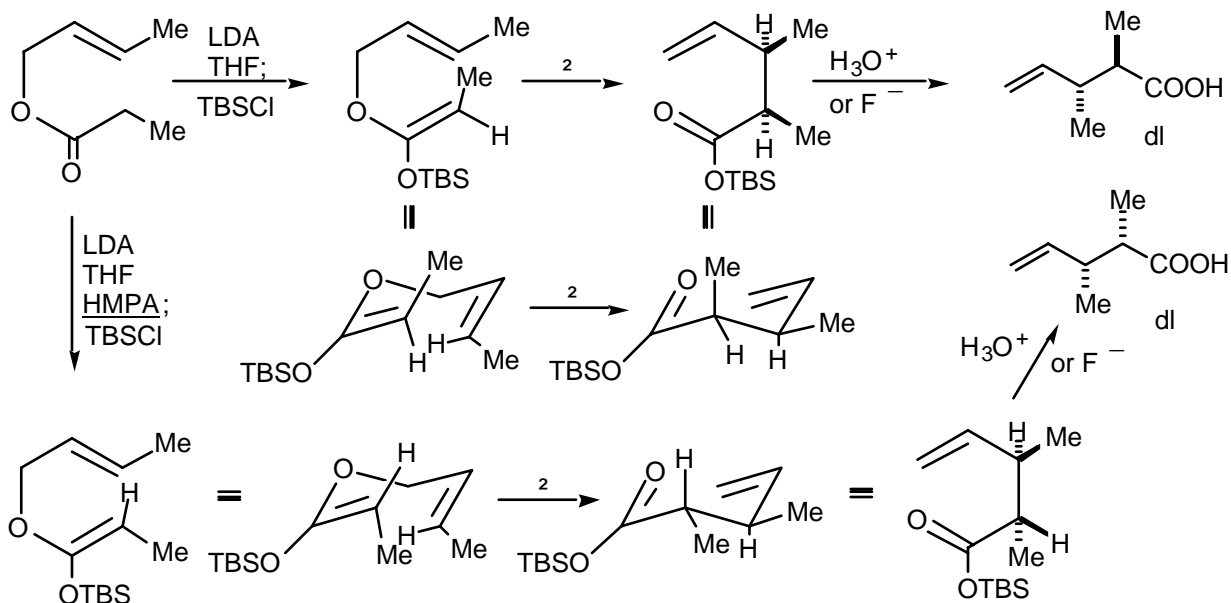


in less coordinating solvent,
e.g., THF, O-Li is important

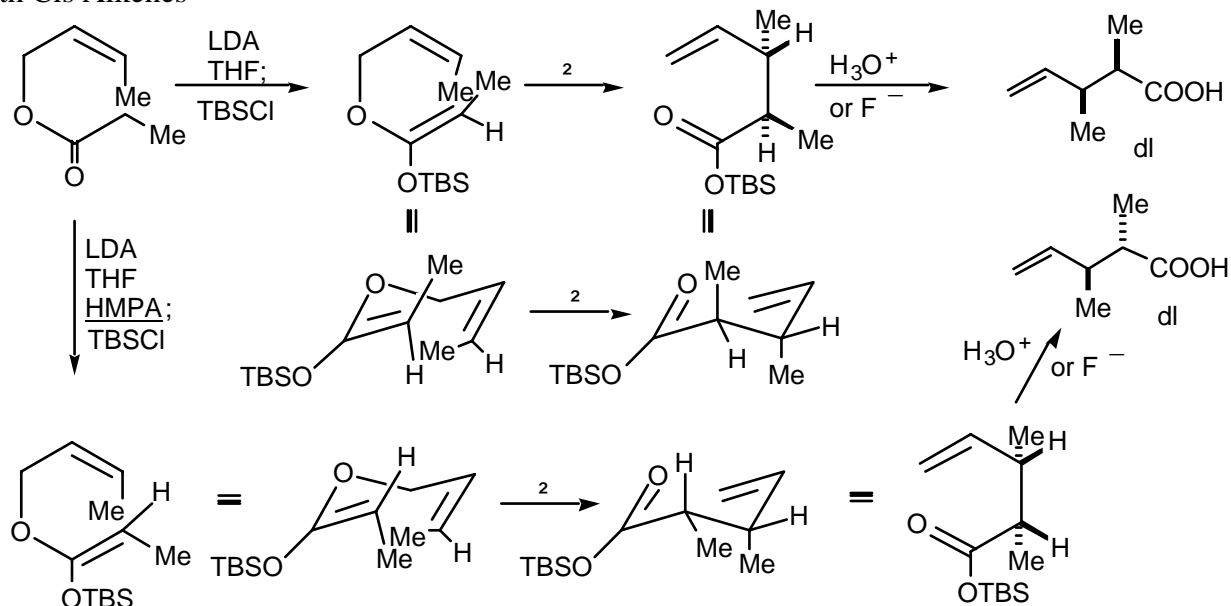
here R' eclipsing O rather
than eclipsing OR

Use of Ester Enolate Claisen For Acyclic Stereocontrol

With Trans Alkenes



With Cis Alkenes



Obviously the two processes can be combined, namely substitution α -to the oxygen and substitution on the double bond and enolate. Starting with optically active alcohols then allows for asymmetric induction and optically active products.

