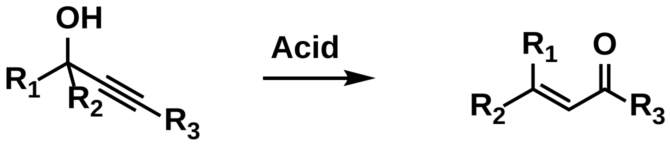
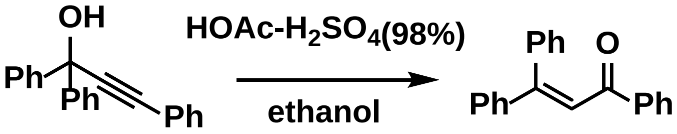
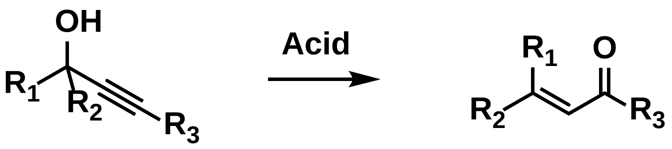
MEYER-SCHUSTER REARRANGEMENT





(Meyer-Schuster,1922)

Chem.Ber.,55,819(**1922**)



R$_1$= *tert*-alkyl,aryl;R$_2$= *tert*-alkyl,aryl;R$_3$= H, electron-donating groups

Acid=Bronsted acid,'soft' Lewis acid

FEATURES

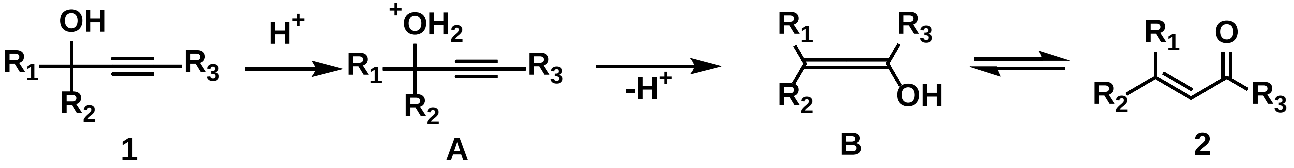
1）when R$_1$,R$_2$= *pri*- or *sec*- alkyl, initial β-elimination of the propargyl alcohol provides an enyne en route to the Rupe product， because the Rupe pathway is typically lower in energy

2）use of “soft” Lewis acid catalysts, which are thought to coordinate preferentially to the alkyne π-system rather than the oxygen atom lone pairs

3）electronic activation of the acetylene to enhance coordination of the Lewis acid catalyst to the alkyne π-system.

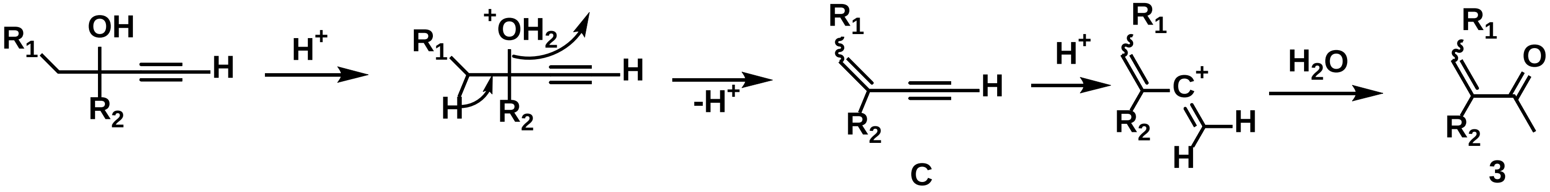
MECHANISM

Meyer-Schuster rearrangement



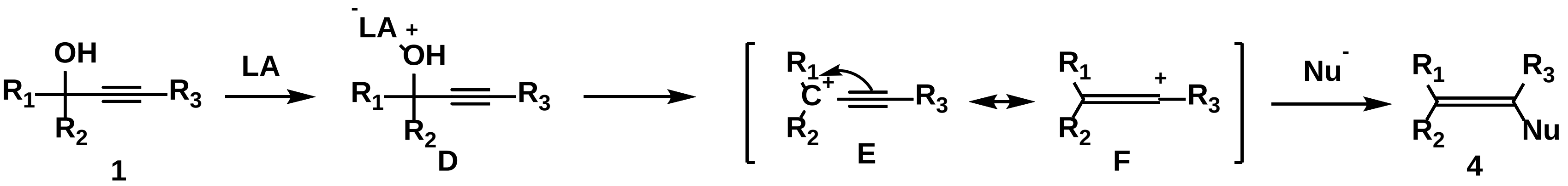
(eq 1)

Rupe rearrangement



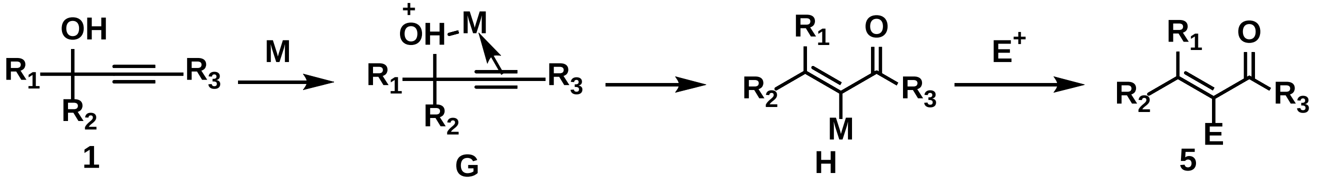
(eq 2)

Allenic carbocation mechanism



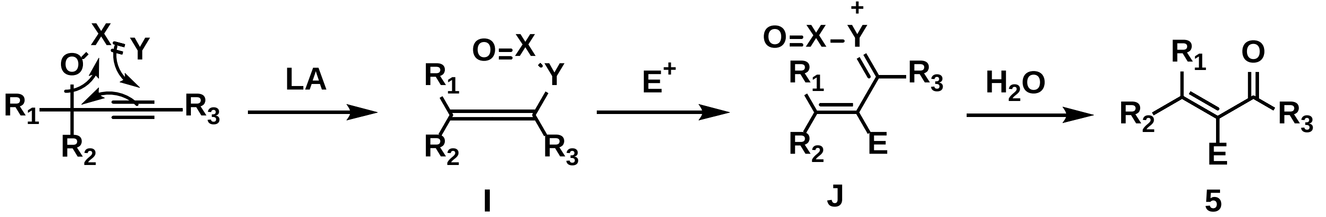
(eq 3)

Carbon-carbon triple activation mechanism



(eq 4)

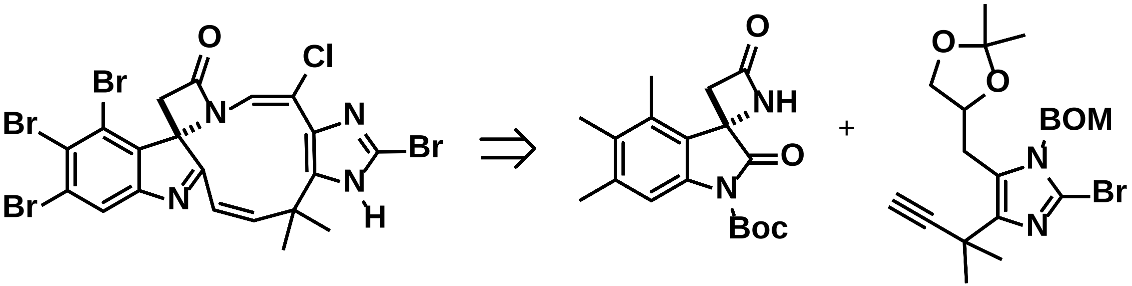
[3,3]rearrangement mechanism



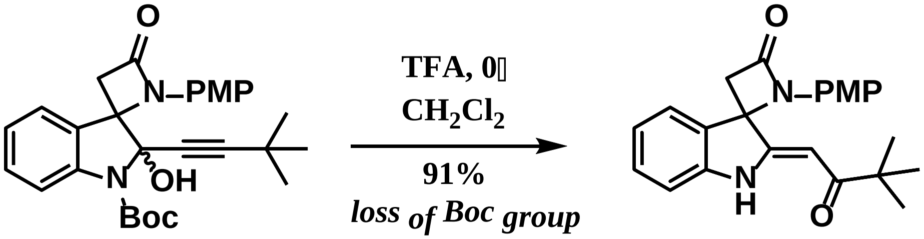
(eq 5)

ACS Catal.**2014**,4,1911-1925

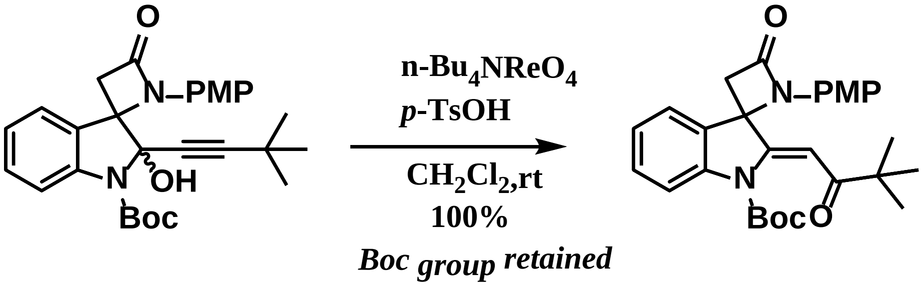
APPLICATION



chartelline A



loss of Boc group



Boc group retained

*J.Org.Chem.***2006**,71,3159-3166