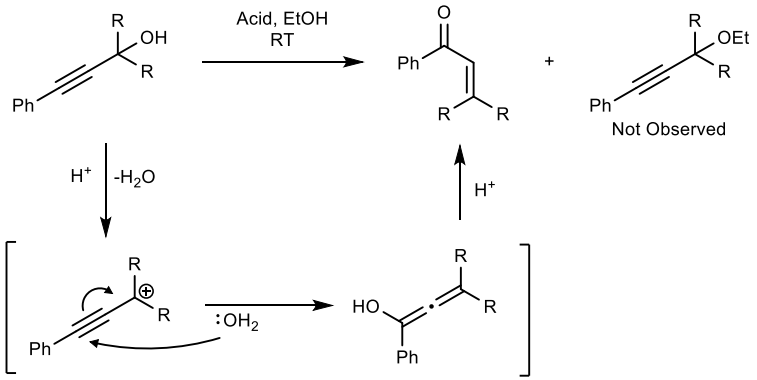
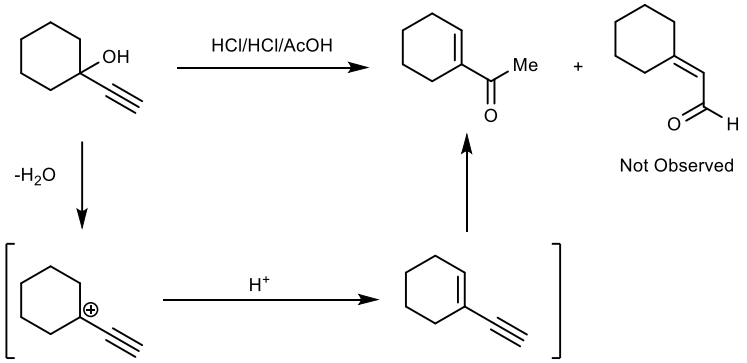
Meyer-Schuster Rearrangement

Historical Perspective

Original Publication –
The expected substitution of a propargylic alcohol with ethanol led to an unsaturated ketone, not the expected ether.



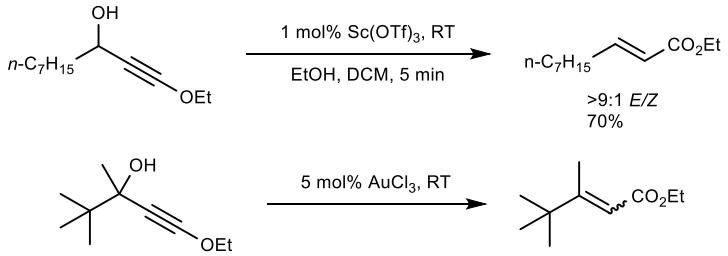
Rupe Rearrangement –
A number of substrates undergo a related Rupe rearrangement instead of the Meyer-Schuster rearrangement.
A lower energy pathway than the M-S rearrangement – beta protons are not tolerated in acid catalyzed M-S.



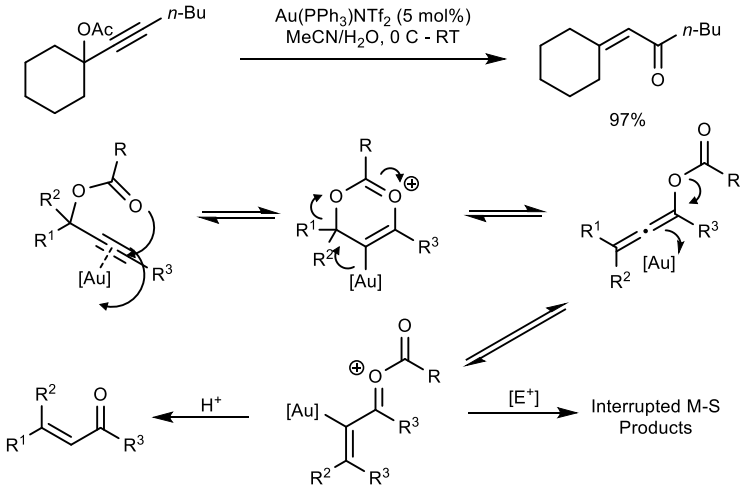
Limitations

1. Rupe Rearrangement is a common side-product
2. No alpha functionality can be incorporated into products.
3. No E/Z stereocontrol of the resultant enone

No More Rupe



Pi-acids activate the alkyne and give good selectivity for the M-S product.



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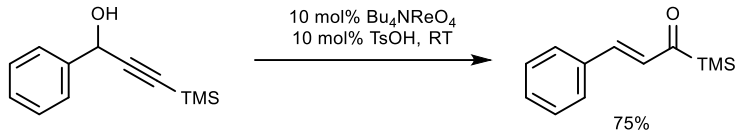
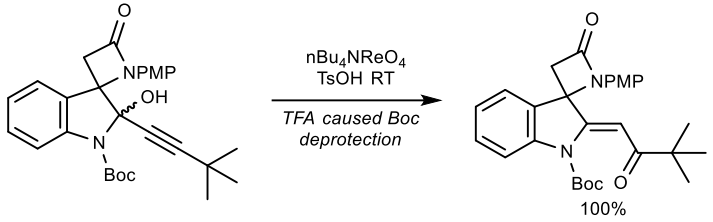
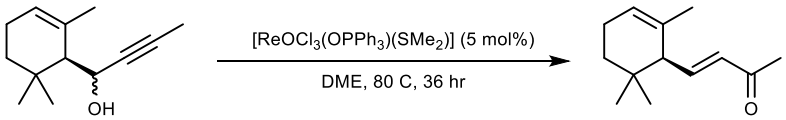
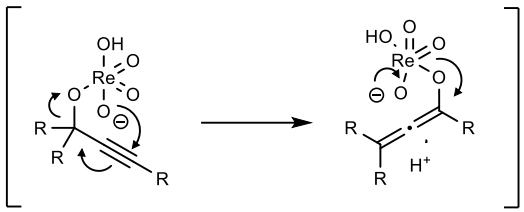
Meyer-Schuster Rearrangement



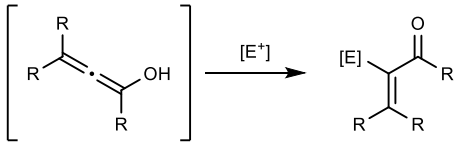




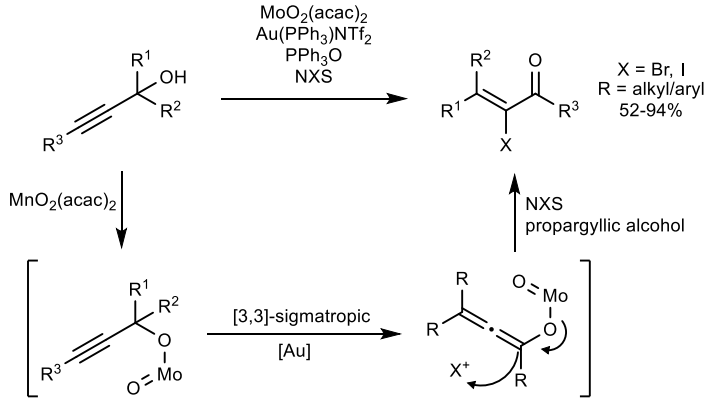


Interrupted M-S

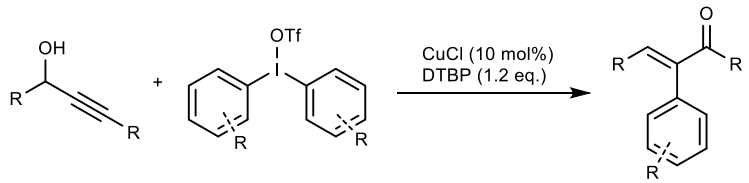
Can the allenic alcohol be utilized to generate alpha functionalized enones?

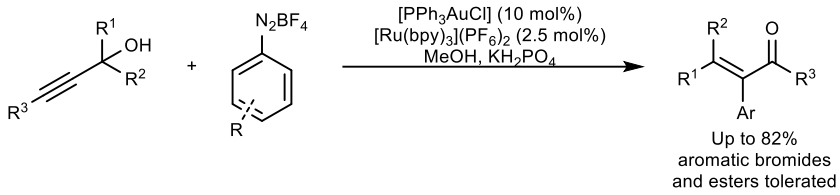


Halogenations

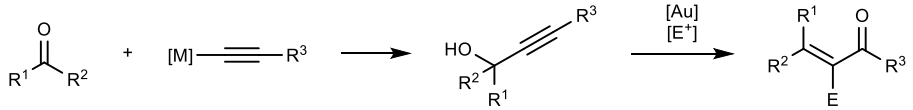


Arylations





Overall



E/Z selectivity still an unsolved problem!