

**B.Sc. Semester-VI
Group A / DSE-4
Organic Synthesis**



**II. Pericyclic Reactions
9. Claisen Rearrangement,**

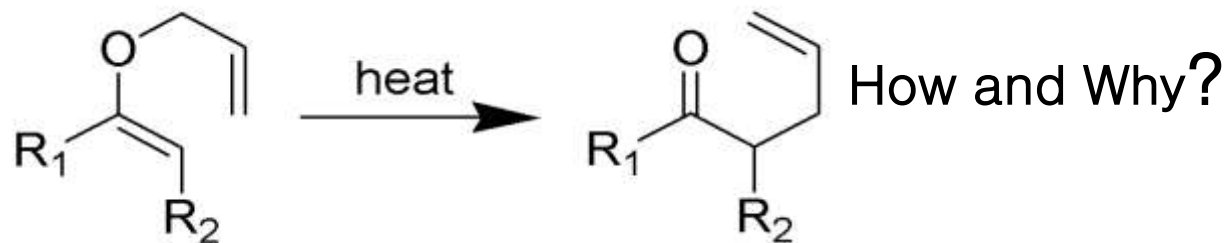


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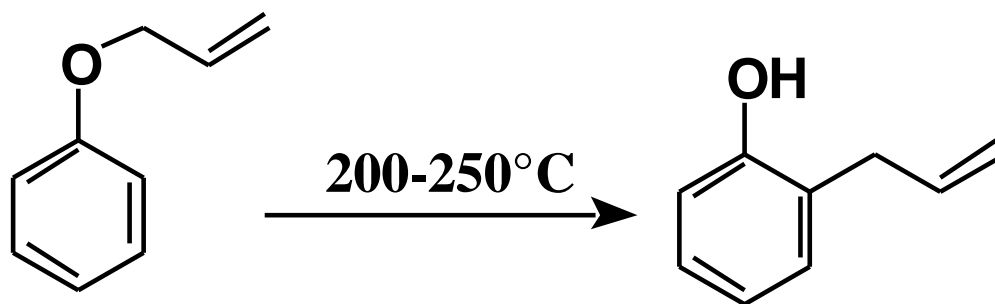
Claisen Rearrangement : [3, 3] Sigmatropic Rearrangement



Rainer Ludwig Claisen
1851-1930

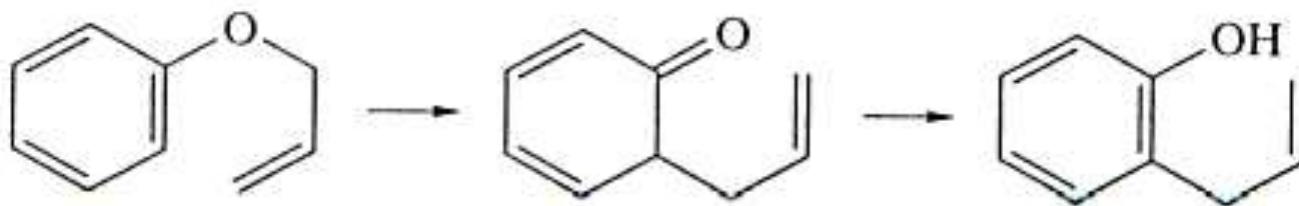


Claisen rearrangement: A thermal rearrangement of allyl phenyl ethers to form 2-allylphenols.



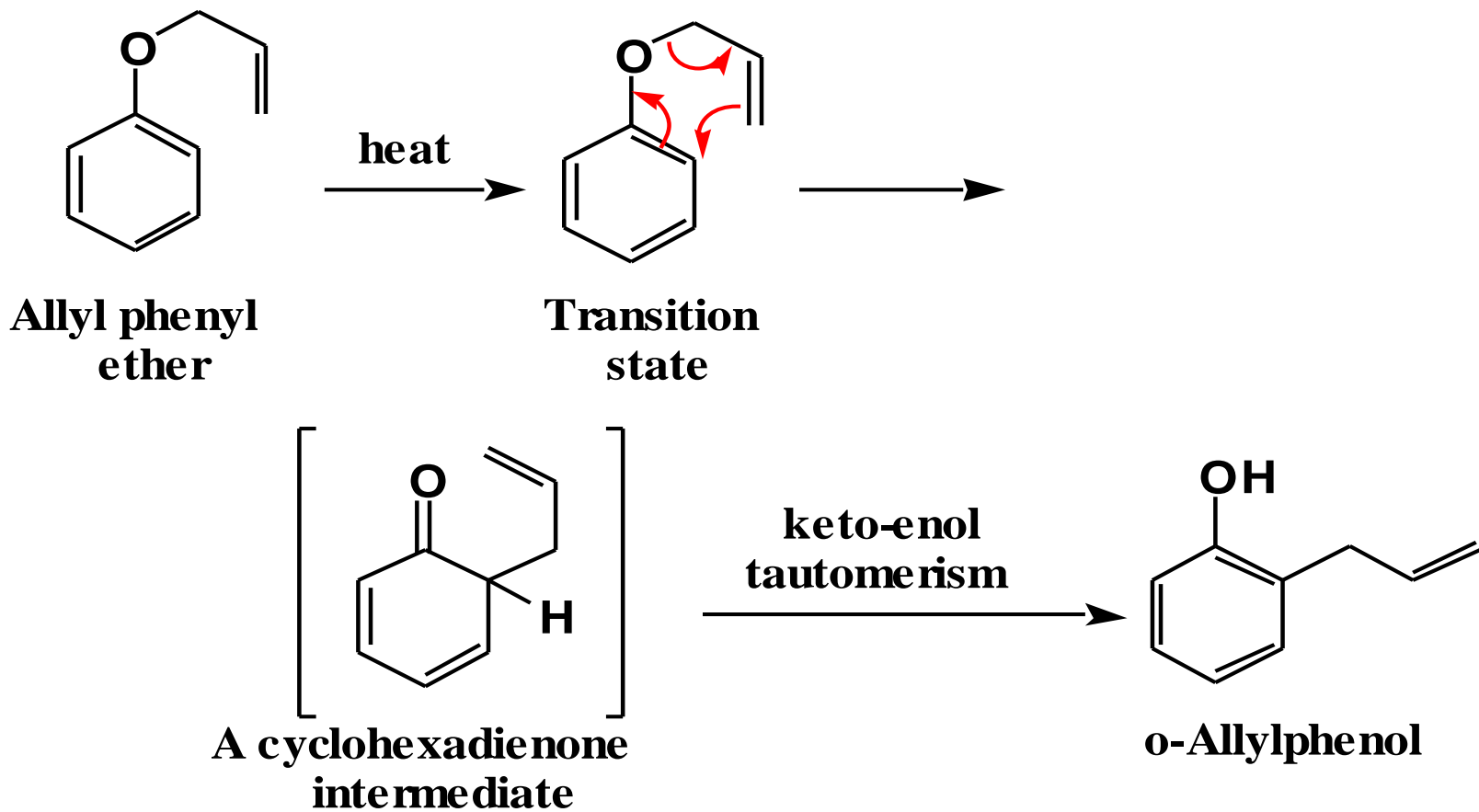
Allyl phenyl ether

2-Allylphenol



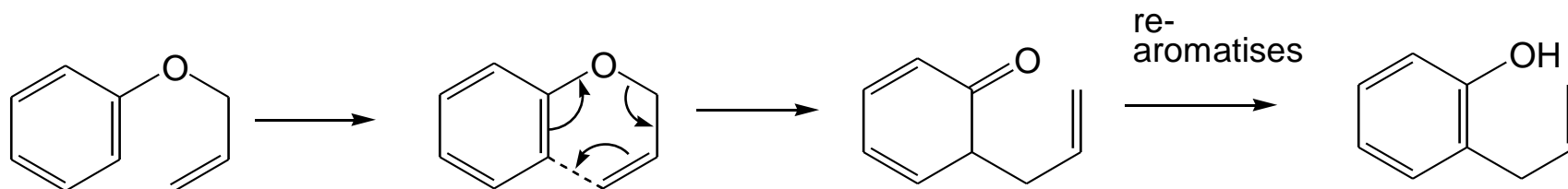
Claisen Rearrangement : [3, 3] Sigmatropic Rearrangement

Mechanism:

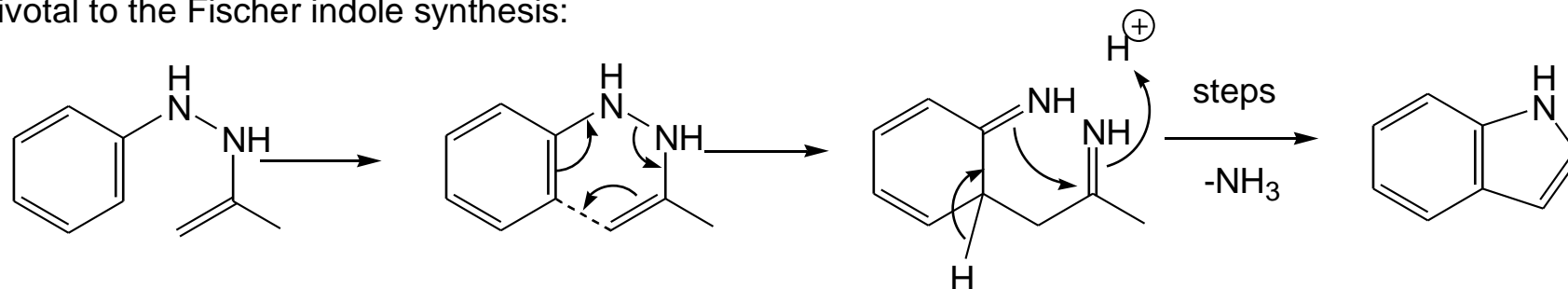


Claisen Rearrangement : [3, 3] Sigmatropic Rearrangement

Claisen reactions are generally irreversible and synthetically useful:



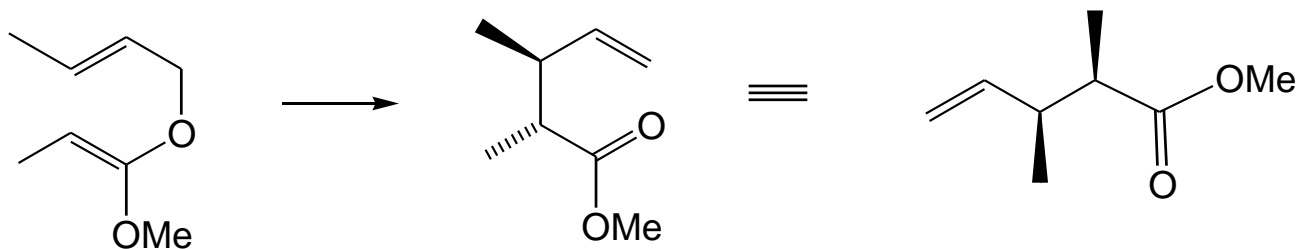
A [3,3]-sigmatropic reaction is pivotal to the Fischer indole synthesis:



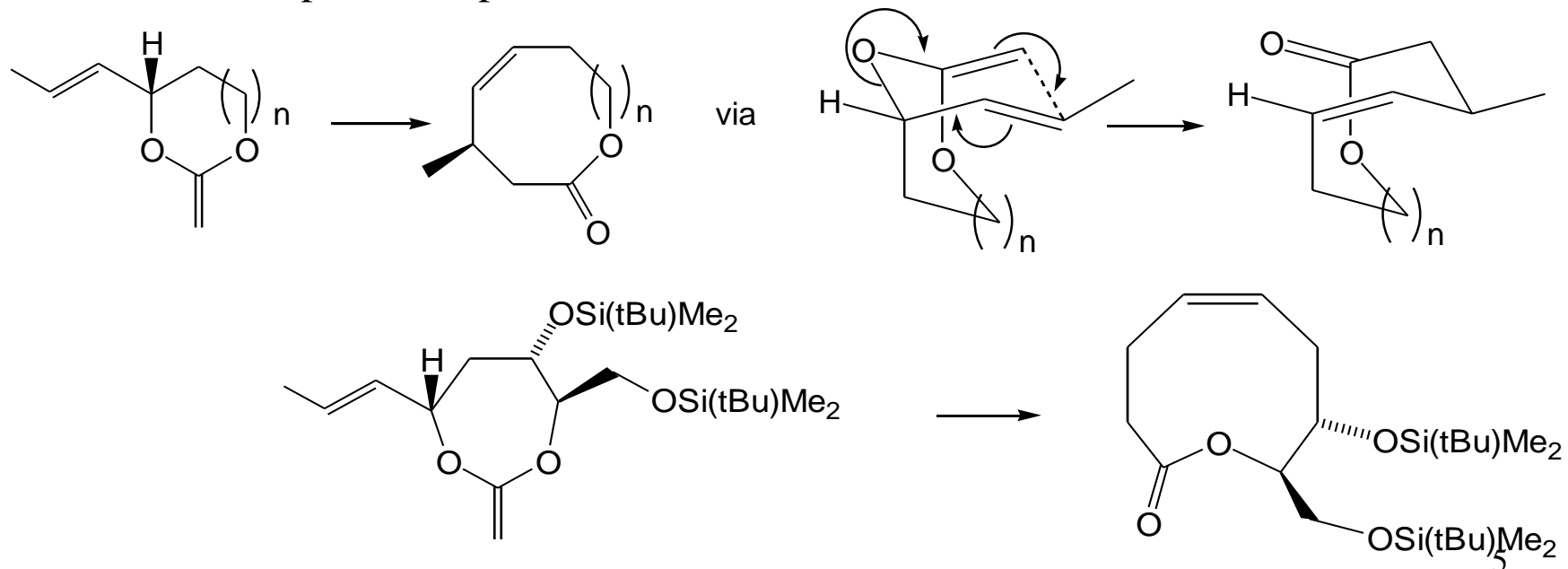
Important: Don't get confused with the Claisen Reactions of esters.

Claisen Rearrangement

The Ireland-Claisen reaction is a useful method for constructing esters, particularly of difficult medium-ring products, with high stereoselectivity.



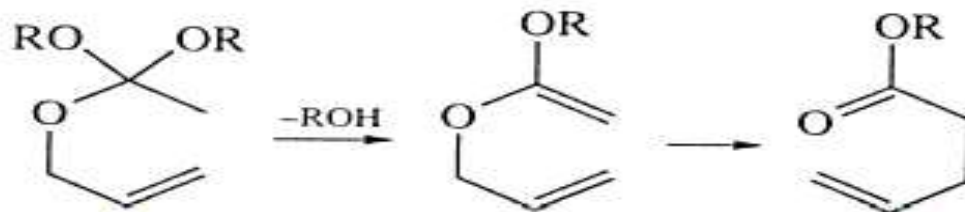
Some more complex examples:



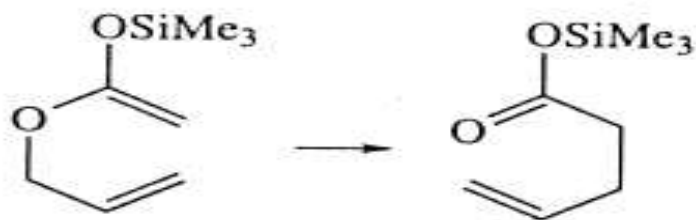
Application to the synthesis of ascidialactone, a marine natural product.

Claisen Rearrangement : Examples

1. Ortho ester Claisen rearrangement



2. Claisen rearrangement of *O*-allyl-*O'*-trimethylsilyl ketene acetals



3. Ester enolate Claisen rearrangement

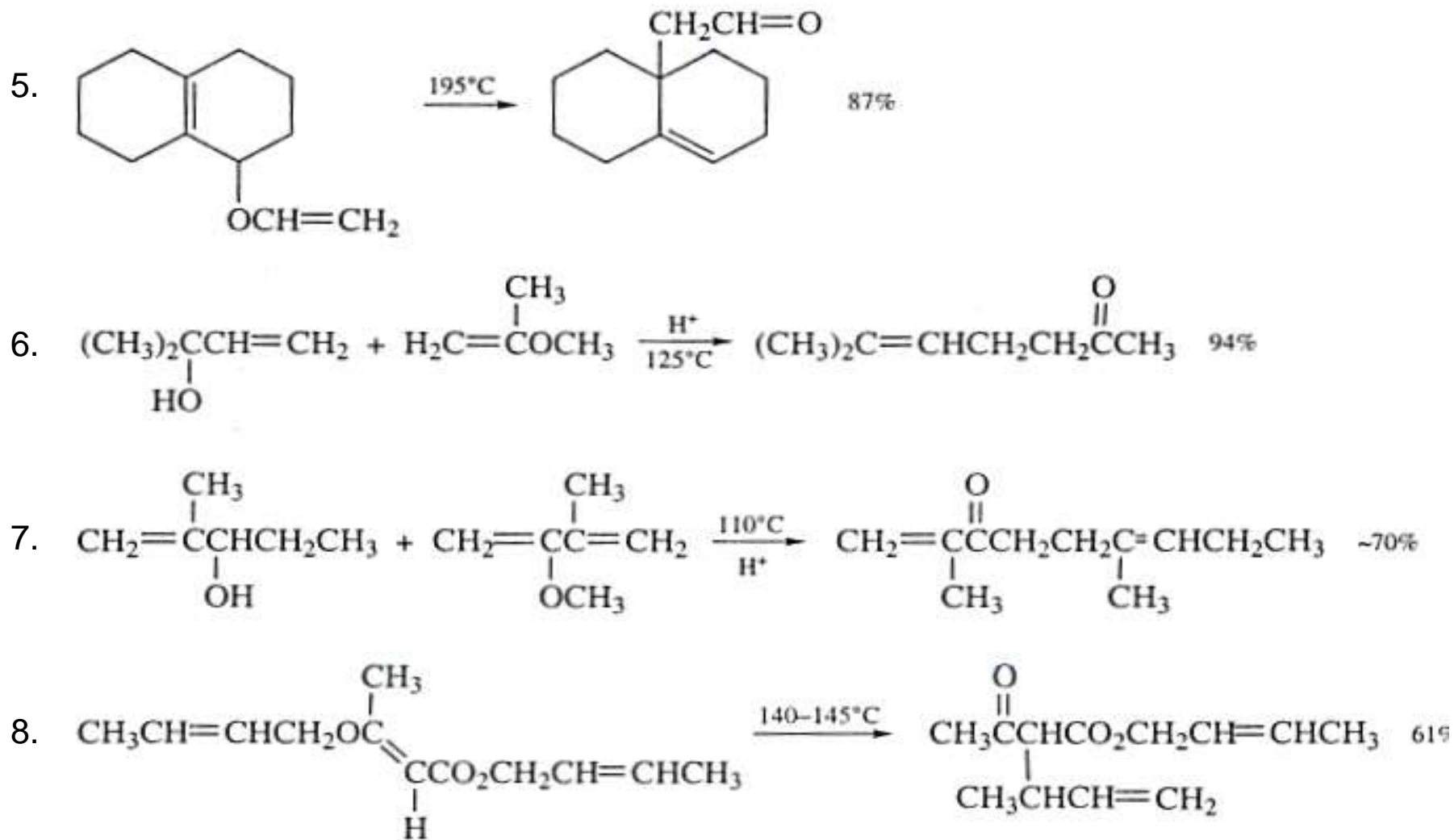


4. Claisen rearrangement of *O*-allyl-*N,N*-dialkyl ketene amins

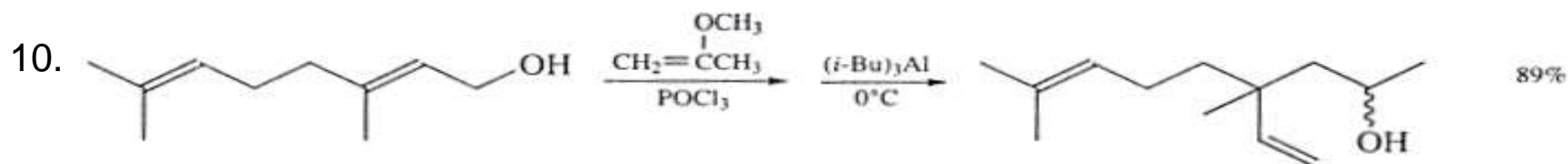
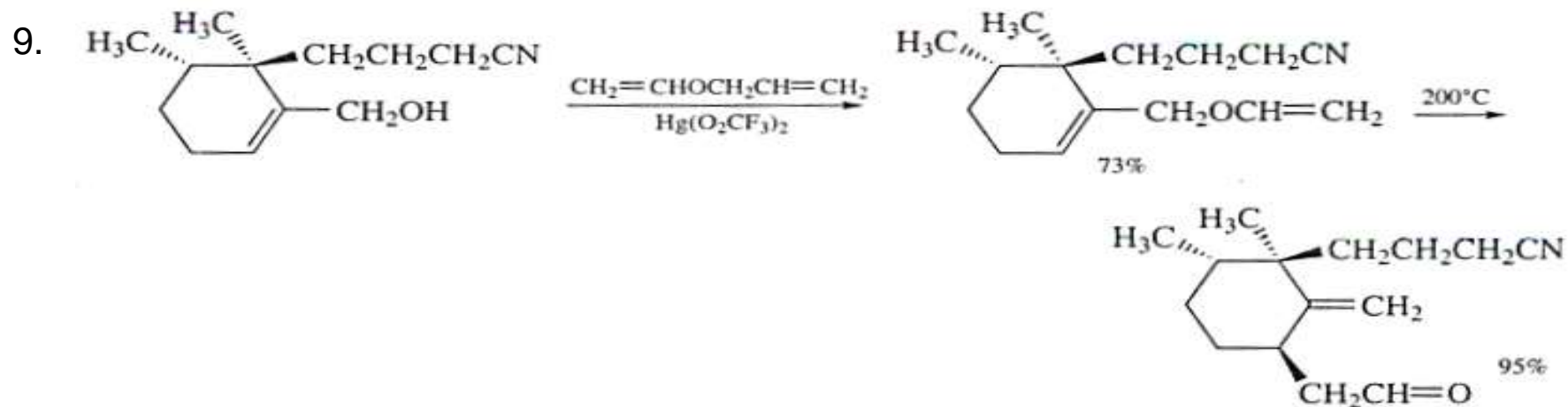


Claisen Rearrangement: Examples

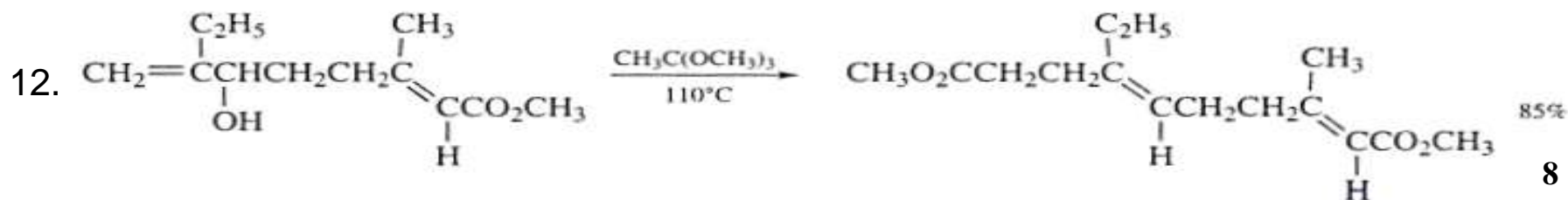
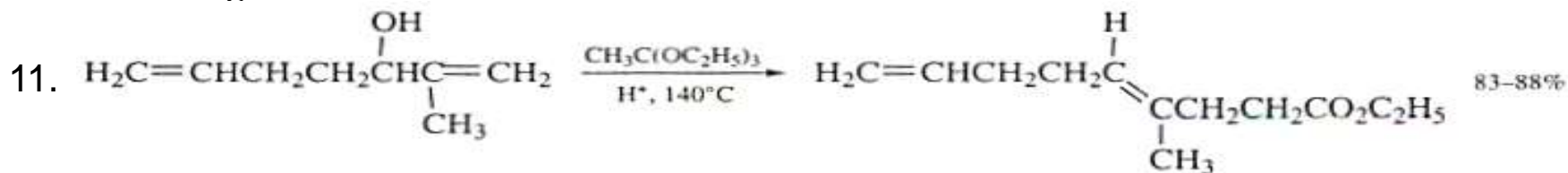
Rearrangement of allyl vinyl ethers



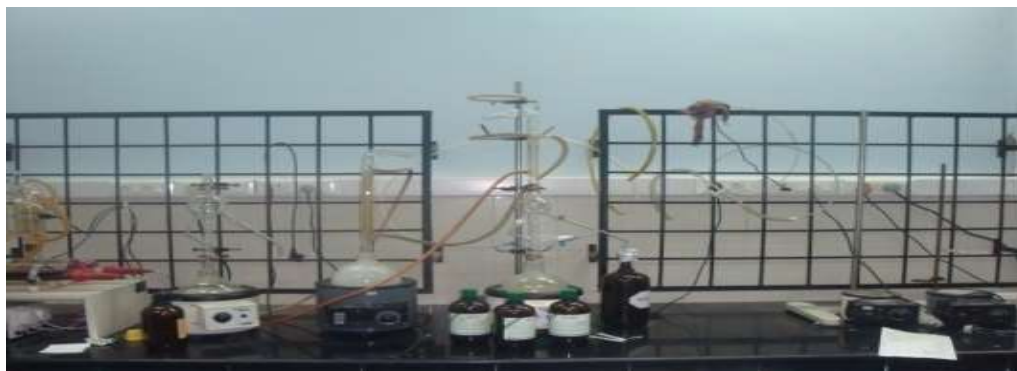
Claisen Rearrangement: Examples



Rearrangement via Ortho Esters



Thank You



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