

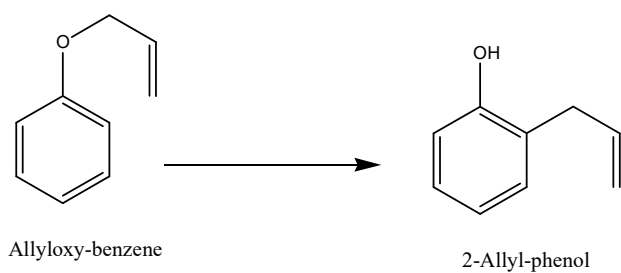
Claisen Rearrangement

First report: Claisen, L. (1912). "Über Umlagerung von Phenol-allyläthern in C-Allyl-phenole". Chemische Berichte. 45 (3): 3157–3166.



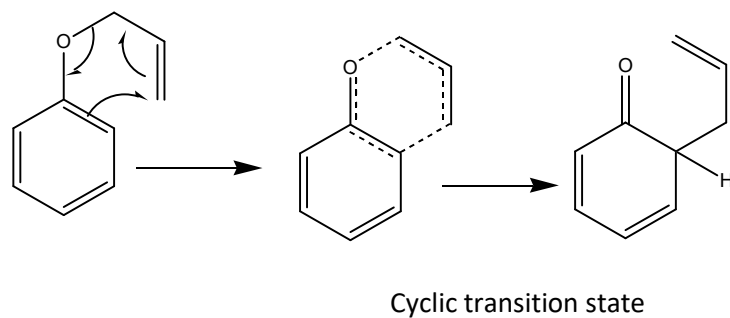
Rainer Ludwig Claisen
(1851 –1930)

Reaction scheme

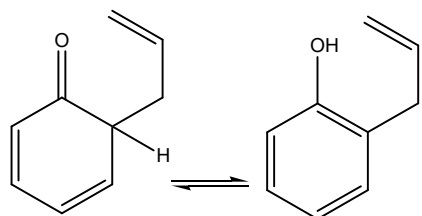


Mechanism

Step 1

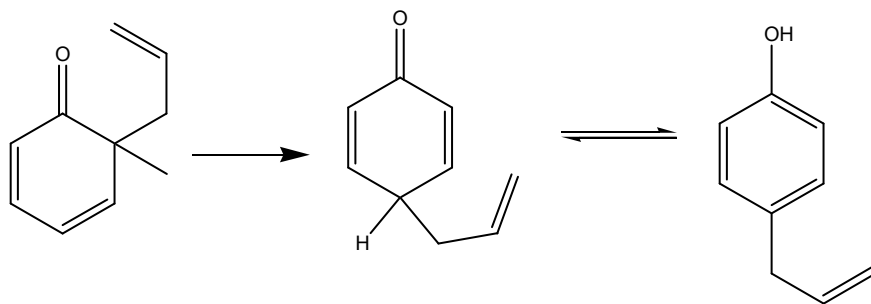


Step 2



Restoration of aromatization

Presence of ortho substituents exclusively leads to para-substituted rearrangement products



Meta-substitution affects

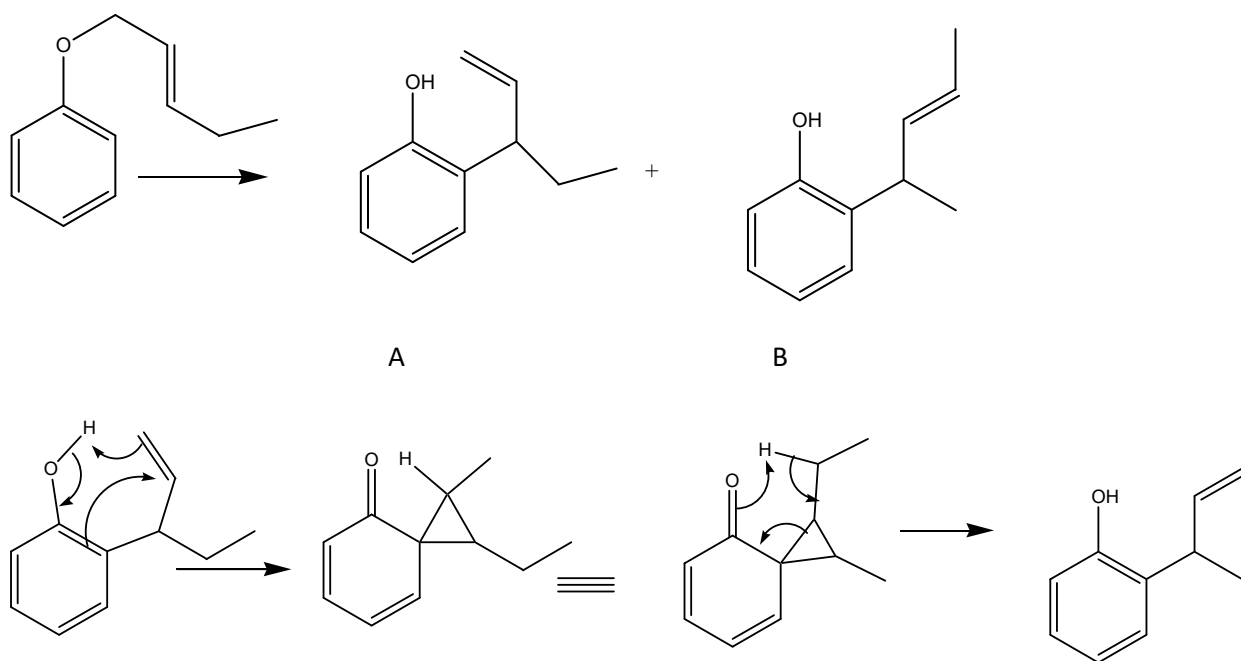
Electron withdrawing groups (such as bromide) direct the rearrangement to the ortho-position

Electron donating groups direct rearrangement to the para-position (69% para product).

Para substituent effect

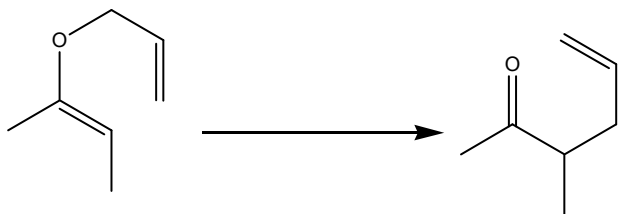
Amino substitution improves rate by 10 times.

Abnormal product



Extension of the reaction:

The heating of an allyl vinyl ether will give a γ,δ -unsaturated carbonyl.



2-Allyloxy-but-2-ene

3-Methyl-hex-5-en-2-one

Application

Preparation of cyclophanes

A **cyclophane** is a hydrocarbon consisting of an aromatic unit (typically a benzene ring) and an aliphatic chain that forms a bridge between two non-adjacent positions of the aromatic ring. More complex derivatives with multiple aromatic units and bridges forming cagelike structures.

