

Fonction et réaction organiques II

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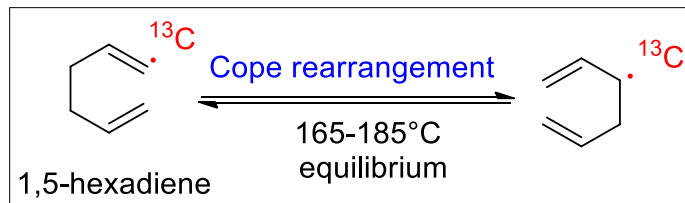
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4.2.1. Cope rearrangement

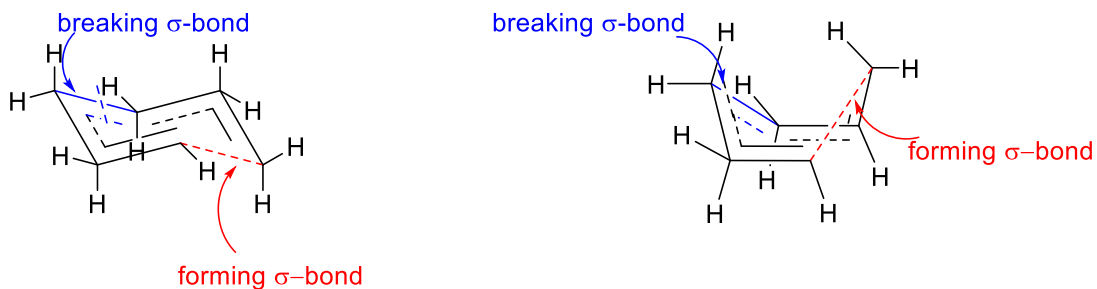
Diels Alder and 1,3-cycloadditions: $4\pi e^- + 2\pi e^-$

Now, concerted molecular rearrangements: $4\pi e^- + 2\sigma$ bonds



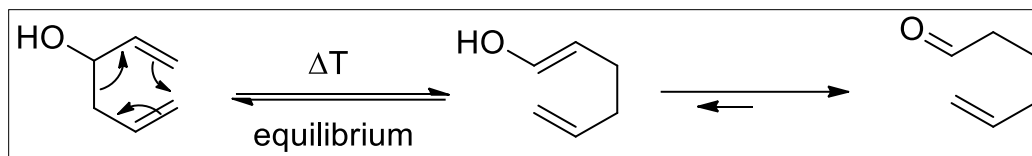
The equilibrium is thermally induced.

The reaction proceeds via a chair or boat transition state:



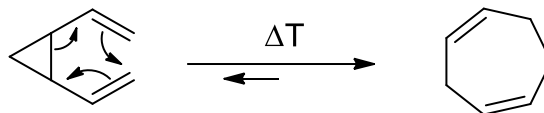
4.2.1. Cope rearrangement

- Driving the equilibrium to one side:
- oxy-Cope rearrangement: driving force = aldehyde formation

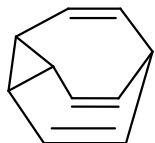


The carbonyl tautomer is more stable, removing the enol from the equilibrium.

- Divinylcyclopropane rearrangement: driving force = release of the ring strain of cyclopropane



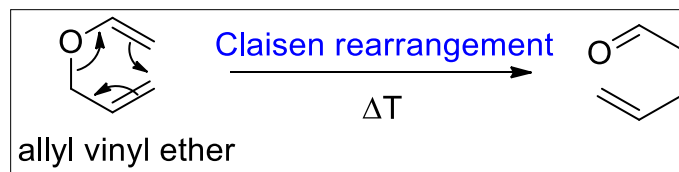
Example: bullvalene



bullvalene

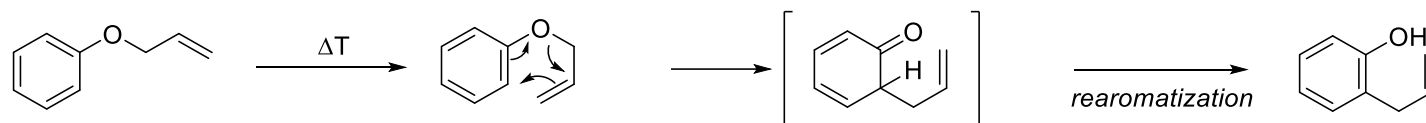
fluxional molecule: degenerated Cope rearrangements lead to different (1'209'600) valence tautomers

4.2.2. Claisen rearrangement

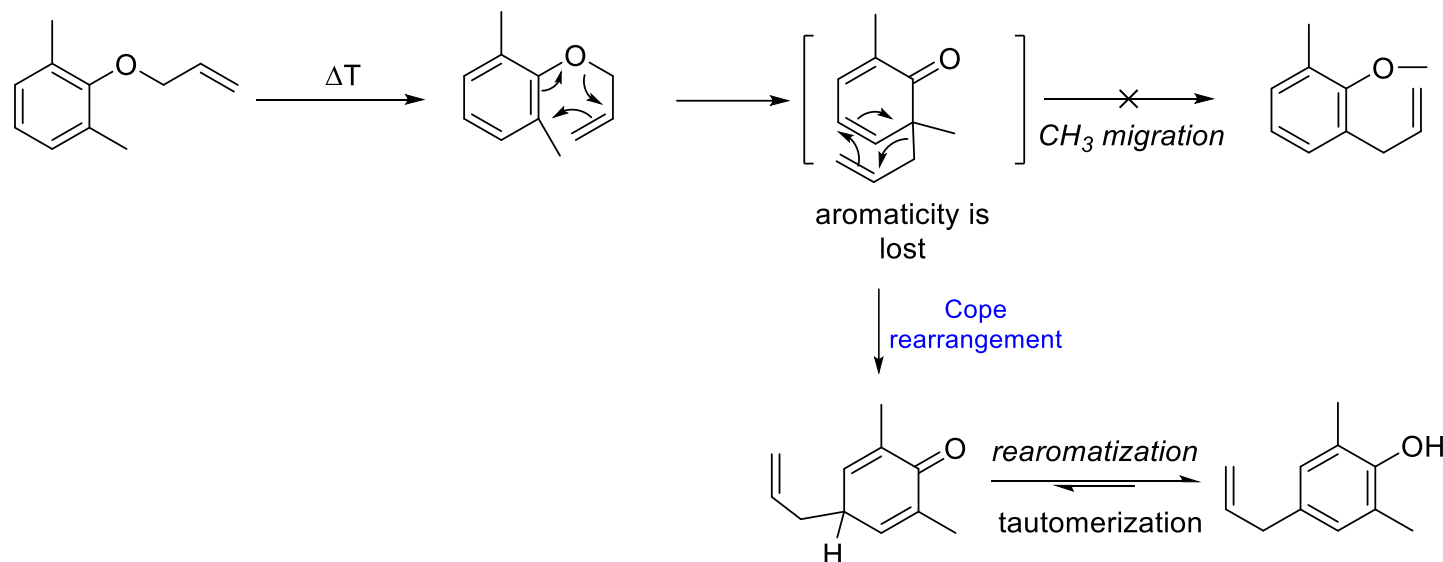


driving force of the reaction = carbonyl group formation

• Aromatic Claisen rearrangement:

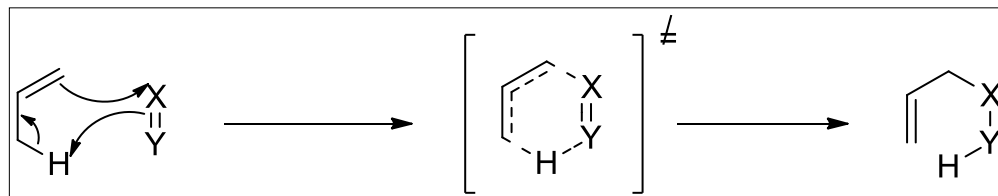


When the ortho-positions are occupied:

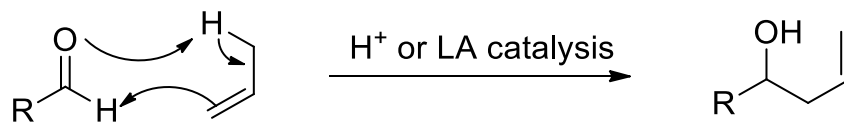


4.2.3. Other rearrangement: the Ene reaction or Alder-Ene reaction

The Ene-reaction is a $2\pi + 2\sigma + 2\pi$ process

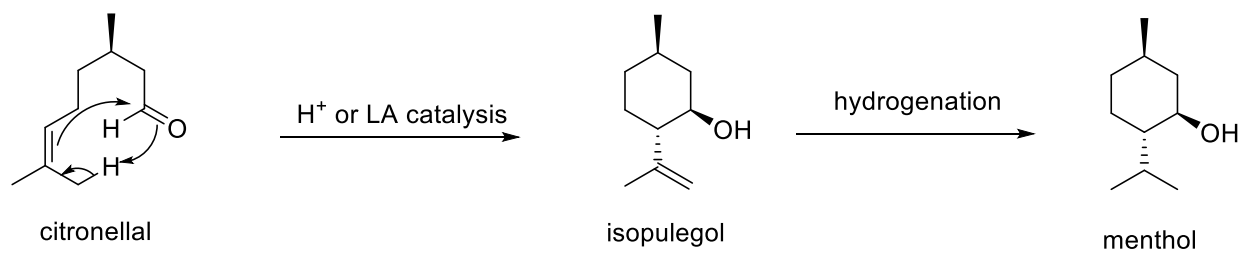
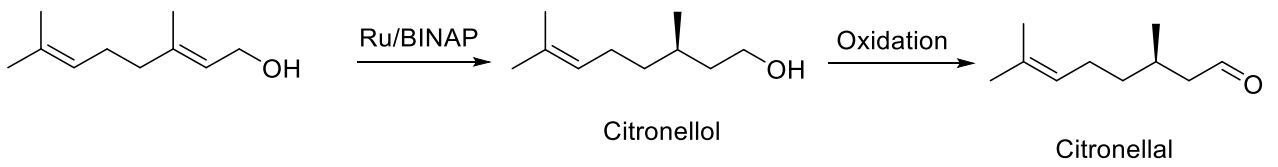
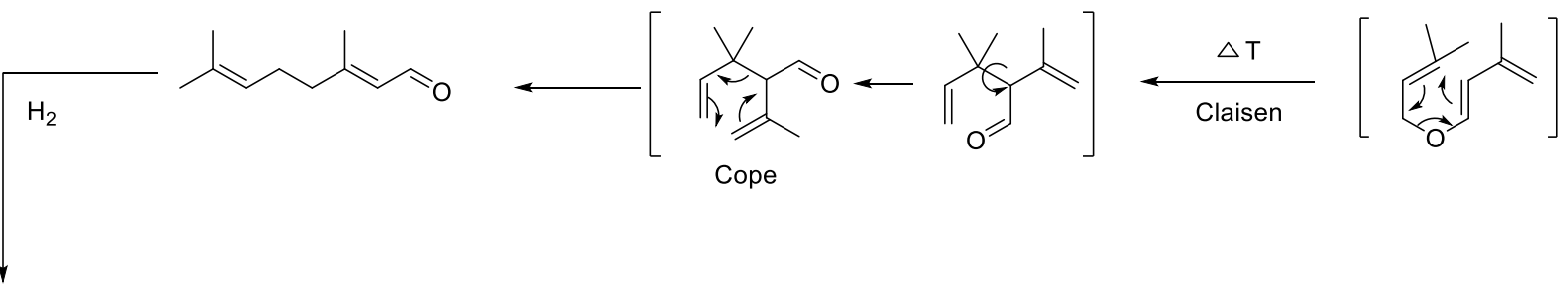
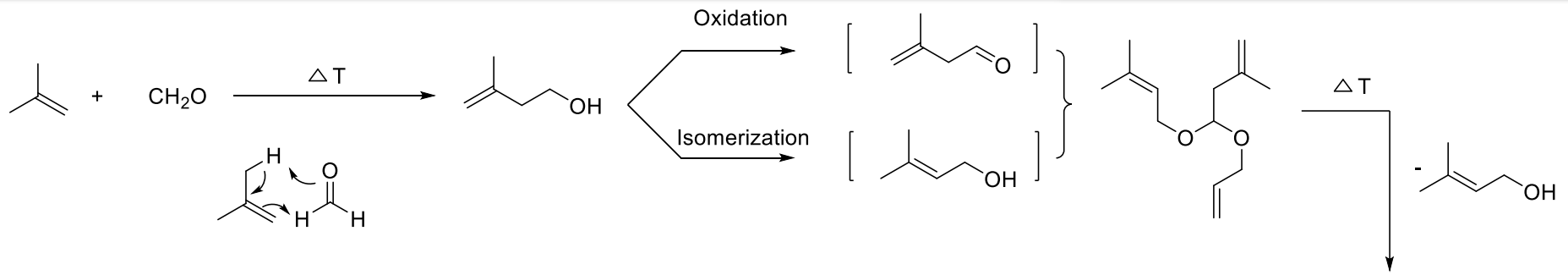


- Important specific example: the carbonyl Ene-reaction



Applied in the technical synthesis of menthol by the Takasago company

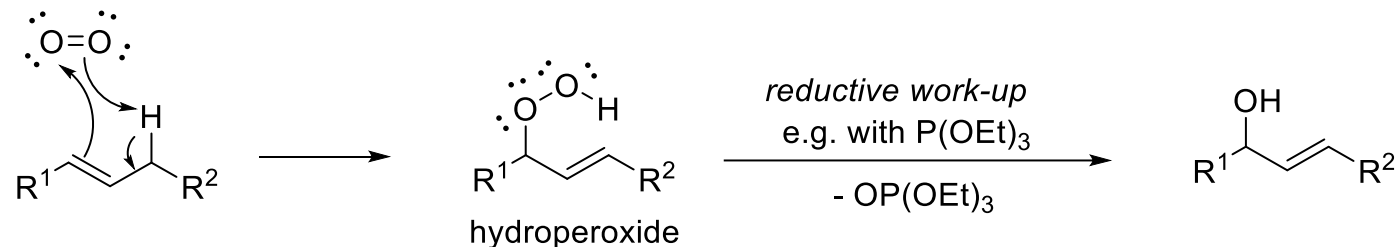
4.2.3. Technical synthesis of menthol (BASF menthol process)



4.2.3. the Ene reaction or Alder-Ene reaction

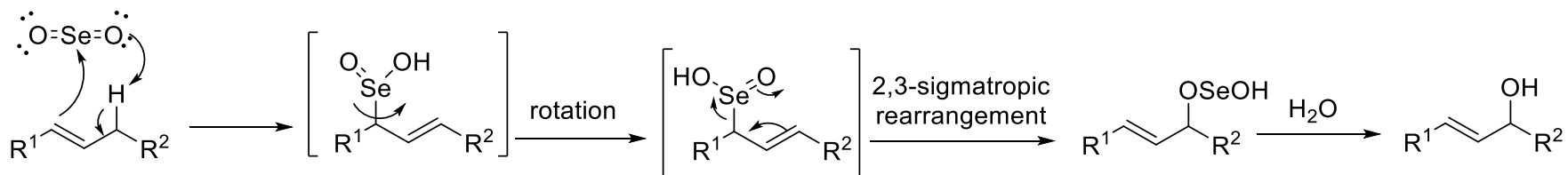
- Ene-reactions with singulett oxygen :

Singulett oxygen is formed by light from “normal” triplett oxygen with a photosensitizer



Overall, this is formally an allylic oxidation with a transposition of the double bond.

- Related reactivity is observed with SeO_2 :



Overall, this is formally an allylic oxidation keeping the position of the double bond.