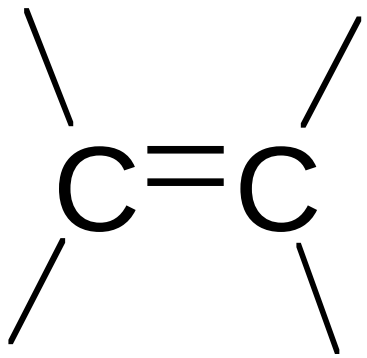
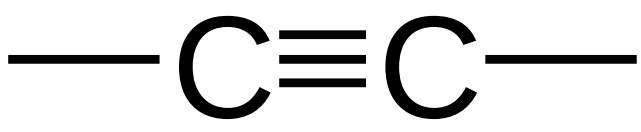
Organic Chemistry Concepts LOKT.09.051

π-bond reactivity

π – bonds



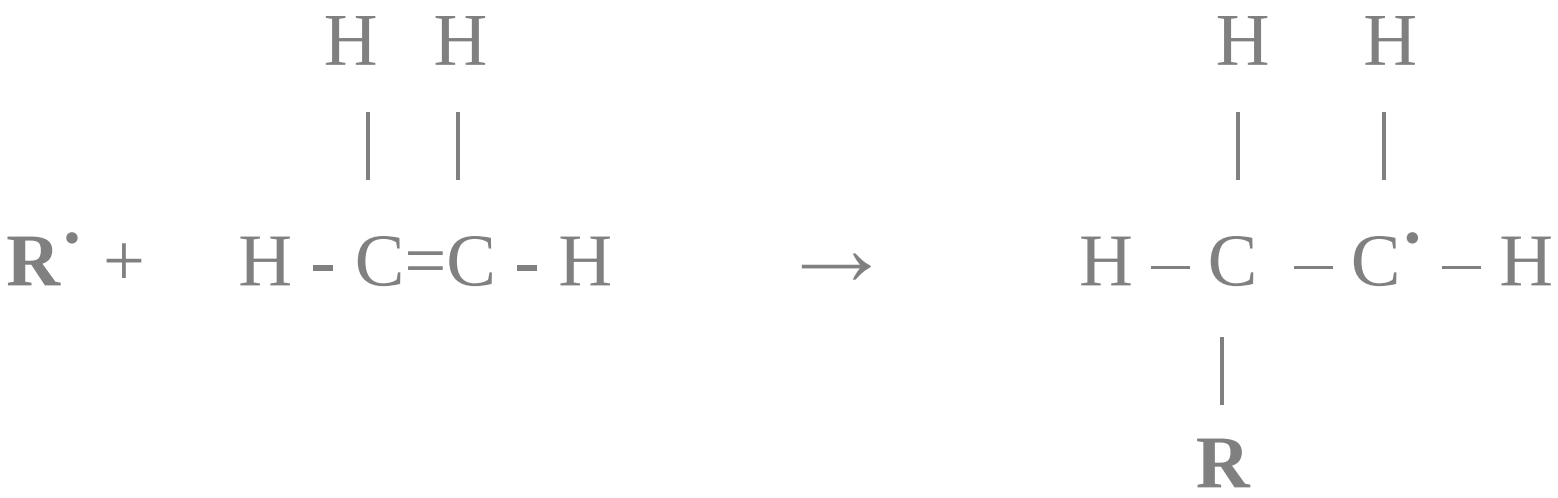


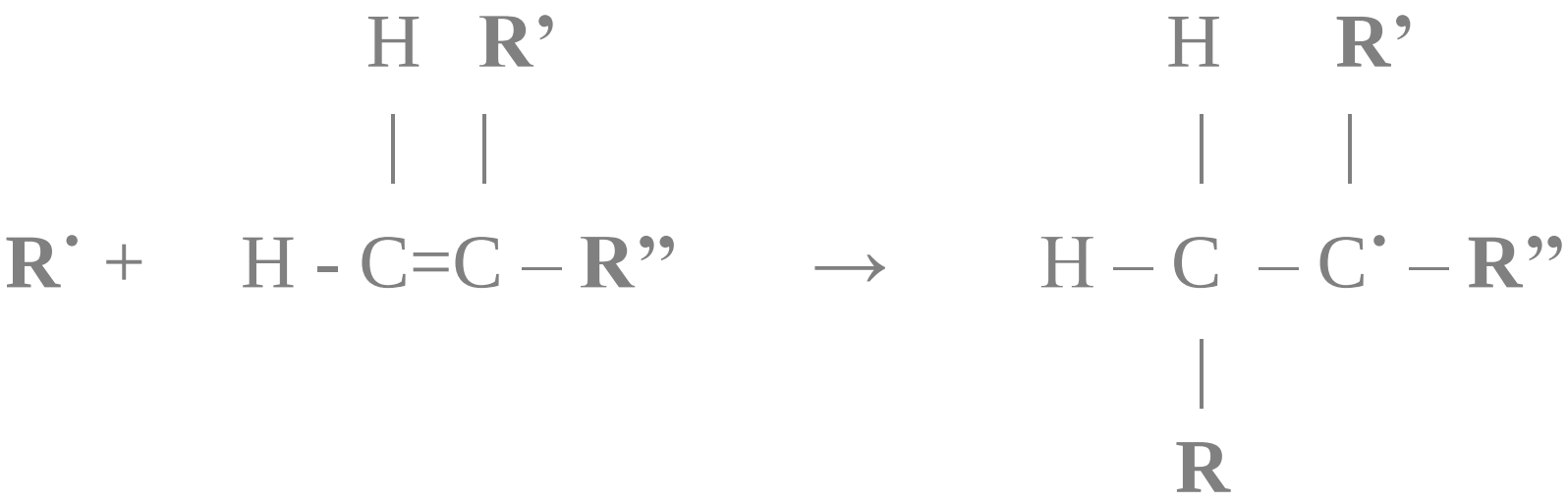
- C – C 83 - 85 kcal/mol
- C = C 146 – 151 kcal/mol
- C ≡ C 199 – 200 kcal/mol

- C – O 85 – 91 kcal/mol
- C = O 173 – 181

- C – N 69 – 75 kcal/mol
- C = N 143 kcal/mol
- C ≡ N 204 kcal/mol

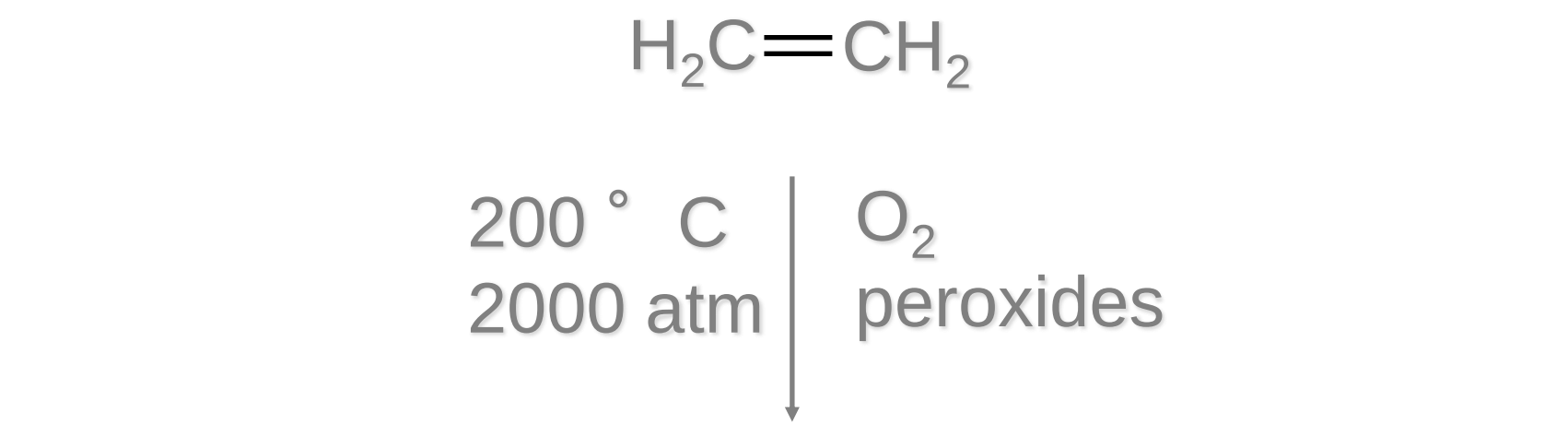
Radical reaction mechanism



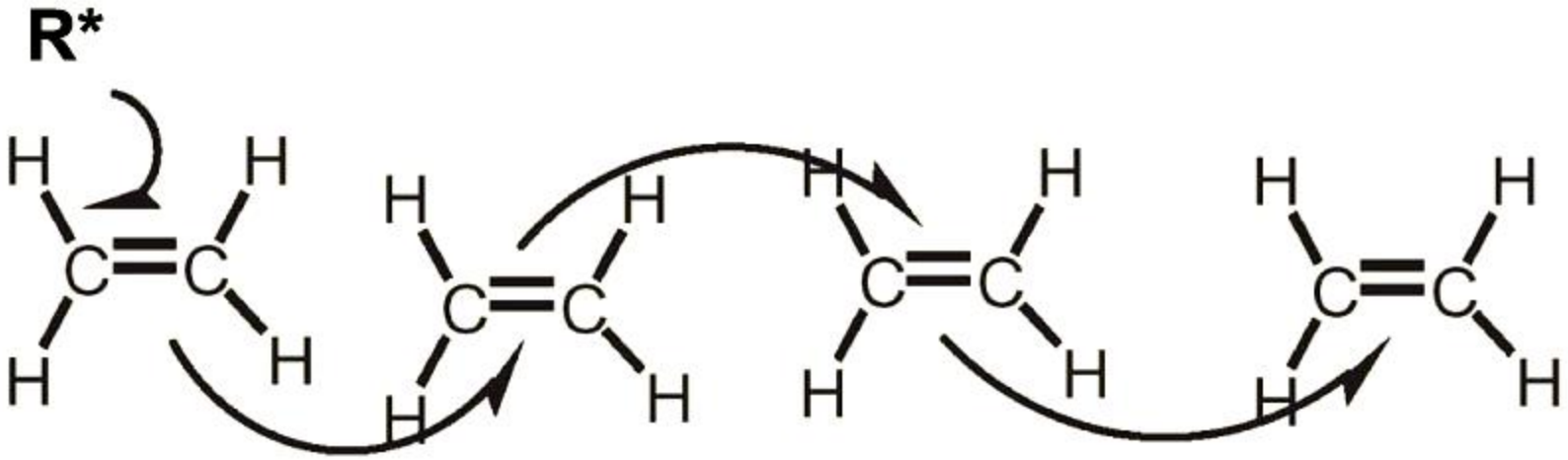


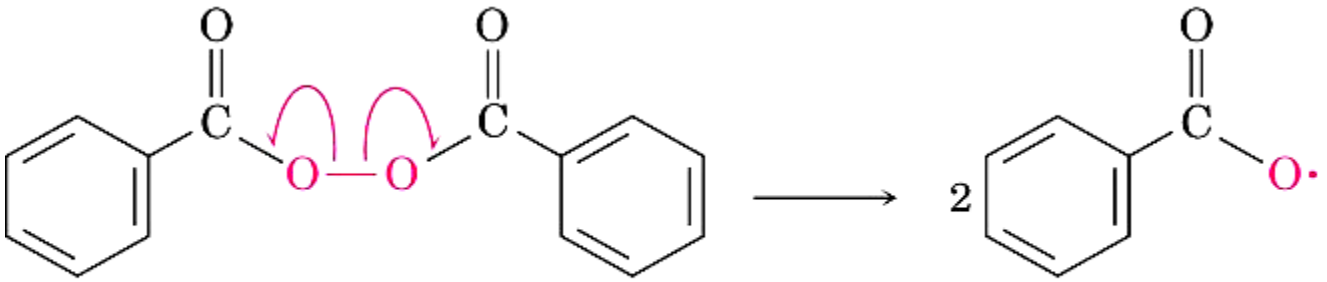
Radical stability determines the reaction center

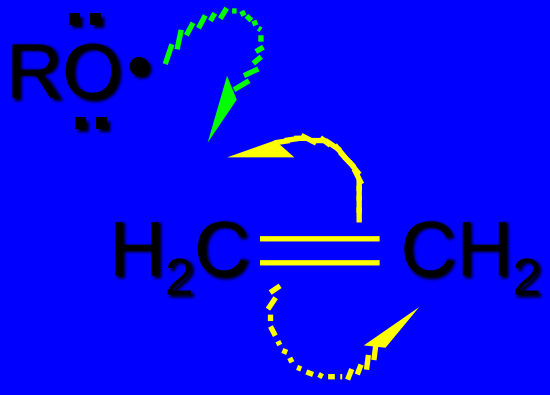
Ethene polymerization

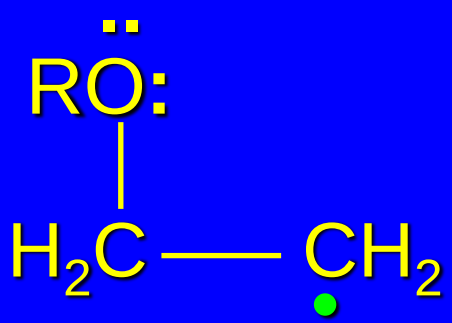


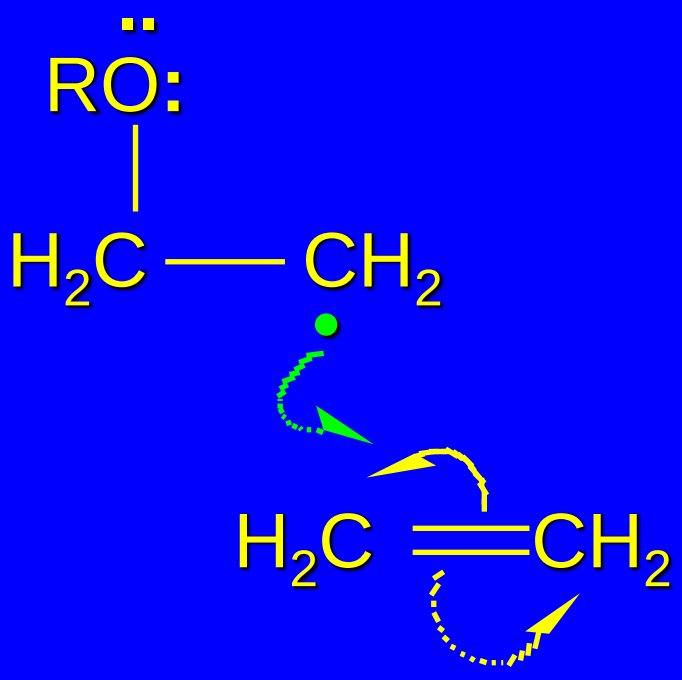
Polyethene or polyethylene

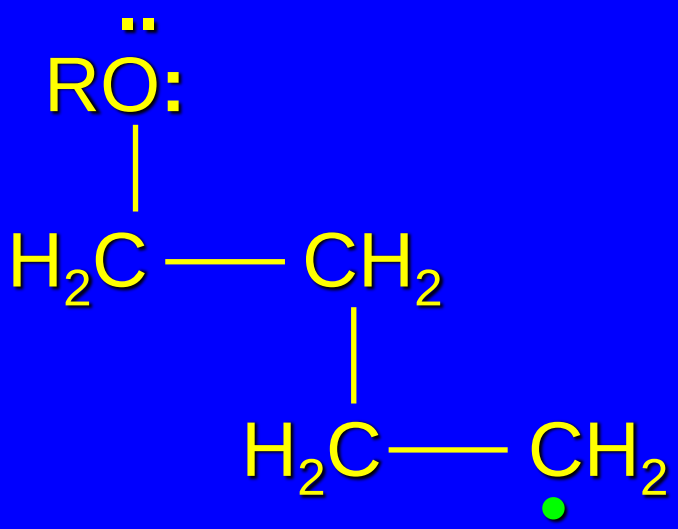

R*
H
C
C
H

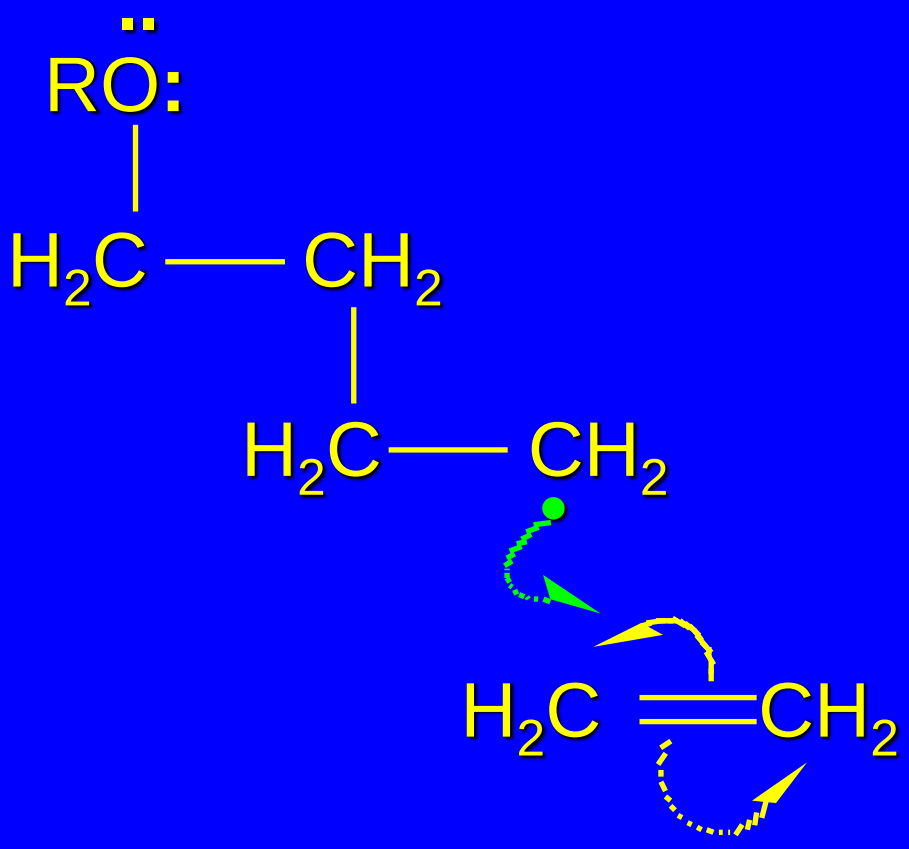

O
C
O
O
2
O·

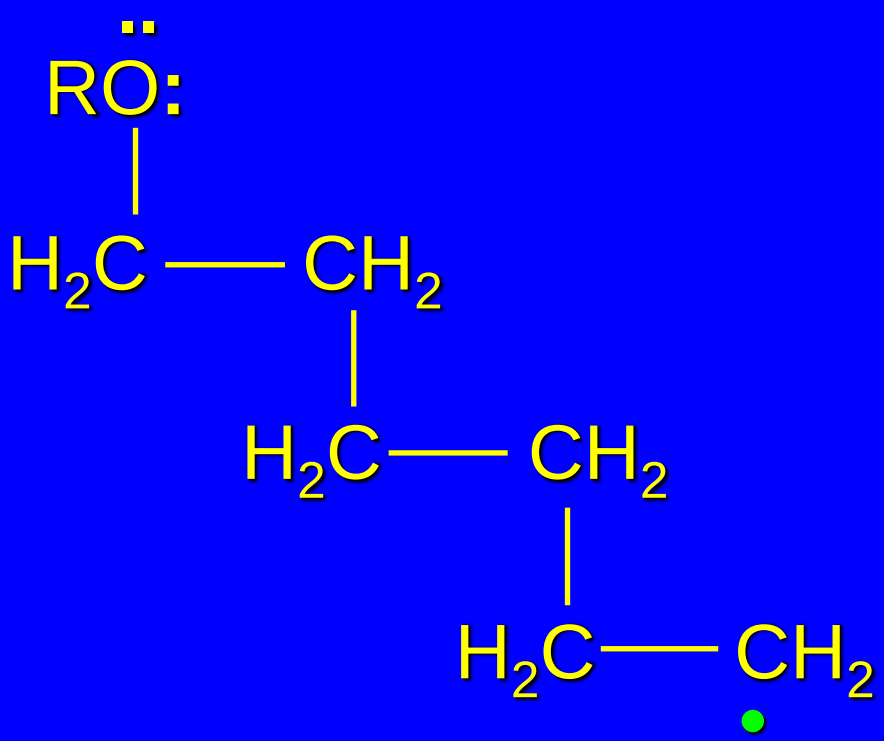

RO
H2C
CH2

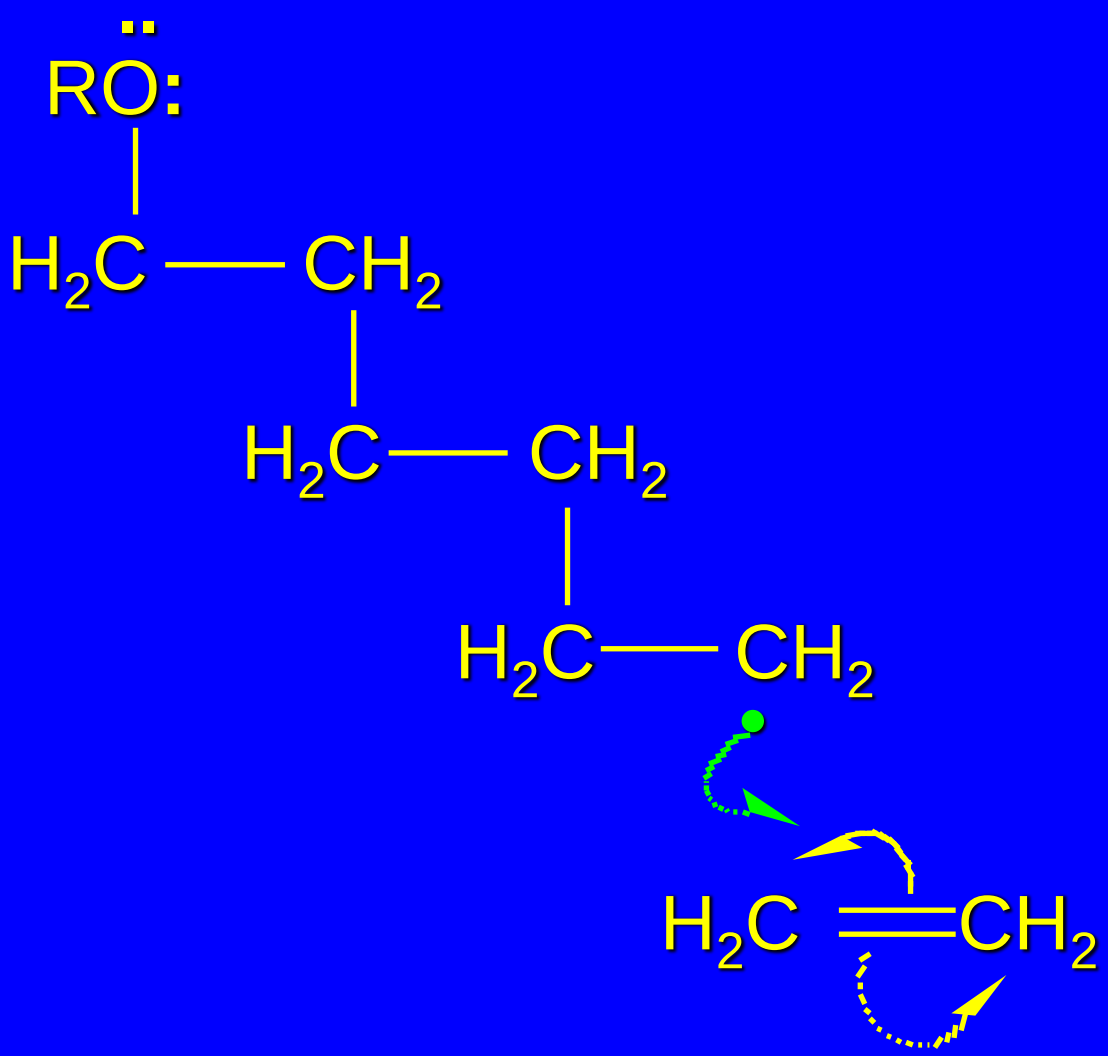

RO:
H2C
CH2


RO:
H2C
CH2
H2C
CH2

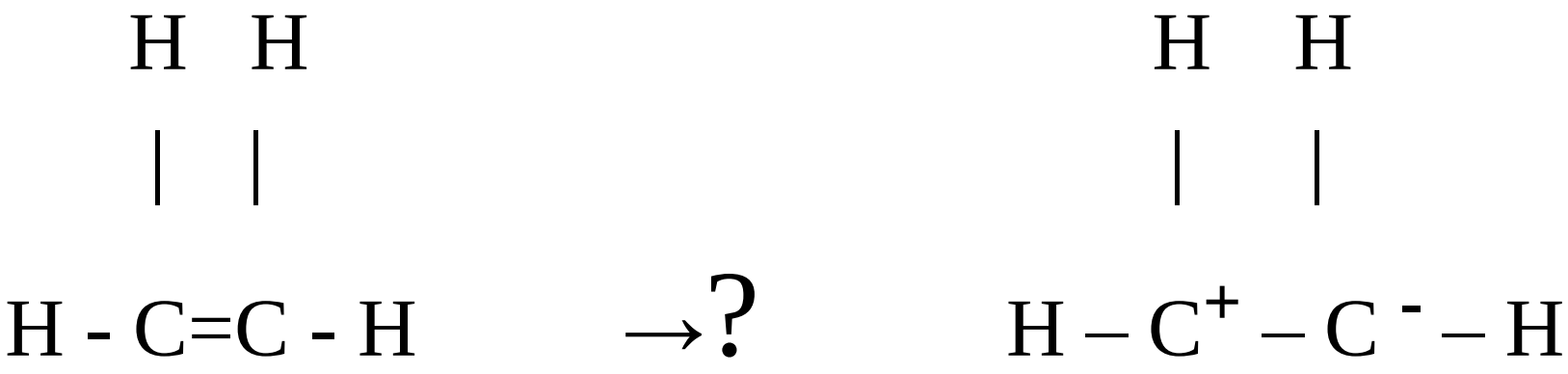

RO:
H2C
CH2
H2C
CH2

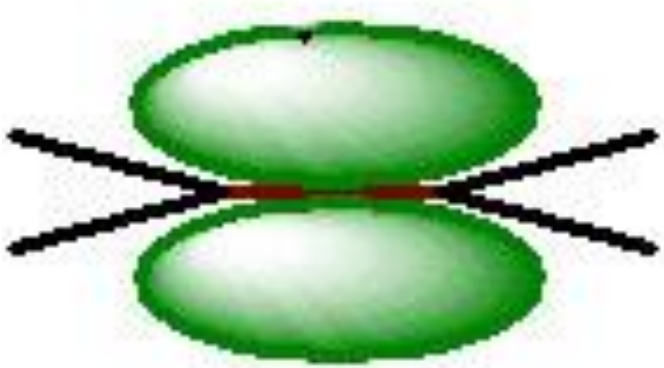

RO:
H2C
CH2
H2C
CH2
H2C
CH2

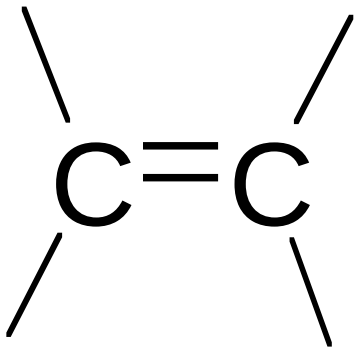

RO:
H2C
CH2
H2C
CH2
H2C
CH2


RO:
H2C
CH2
H2C
CH2
H2C
CH2
H2C
CH2

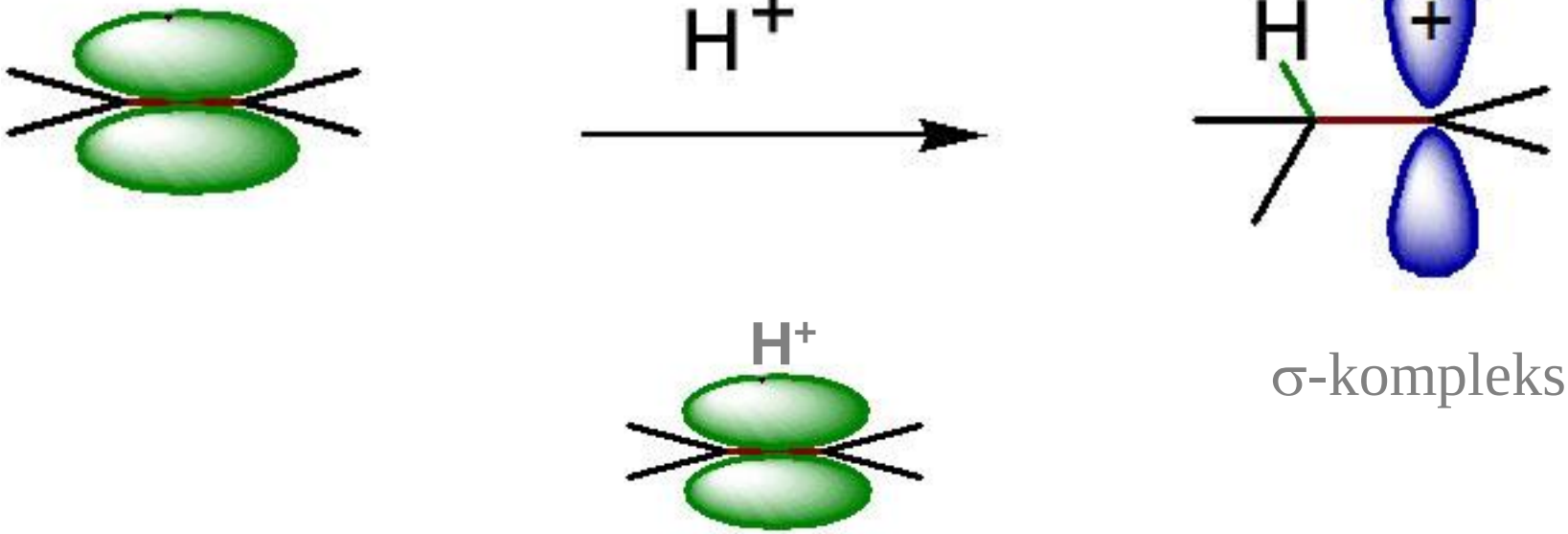
Ionic reaction mechanism





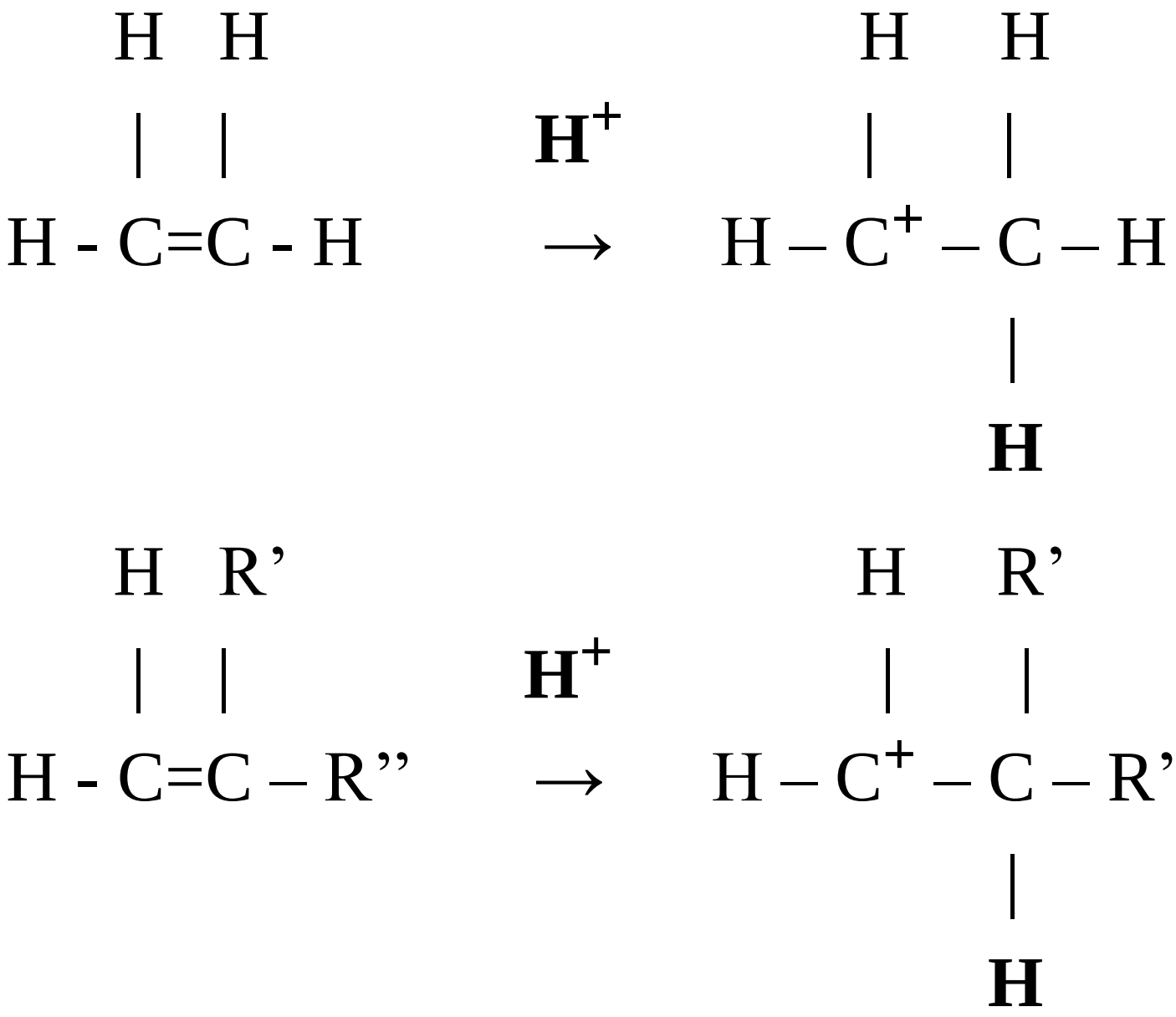

C=C

π- bond as base

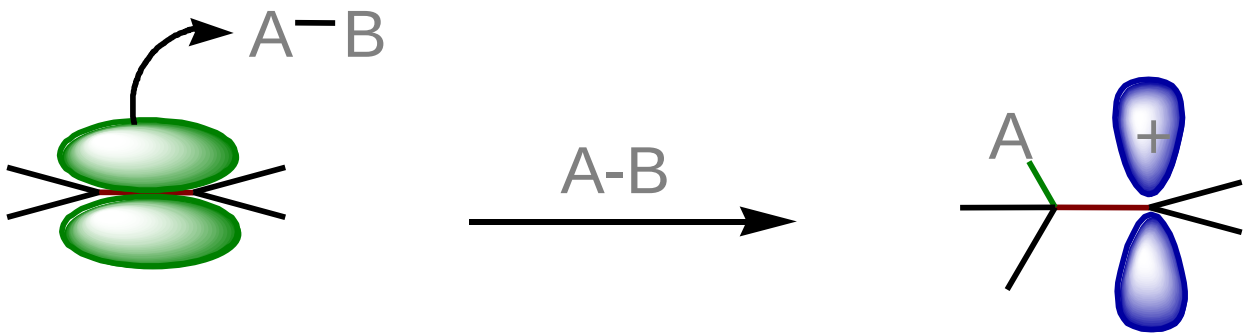


σ-kompleks

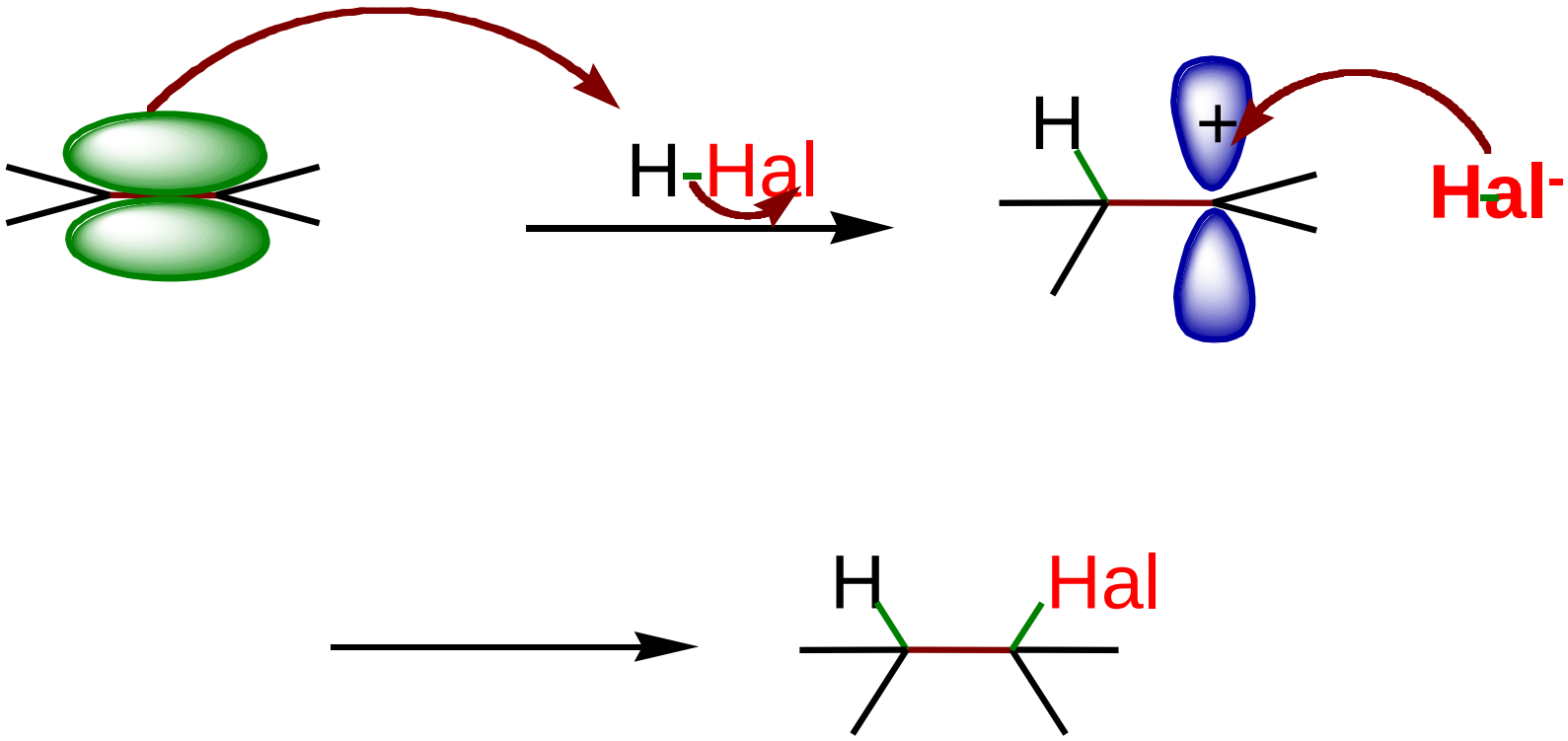
π - kompleks


H H
H - C=C - H
H+
H H
H – C+ – C – H
H
H R’
H - C=C – R”
H+
H R’
H – C+ – C – R”
H

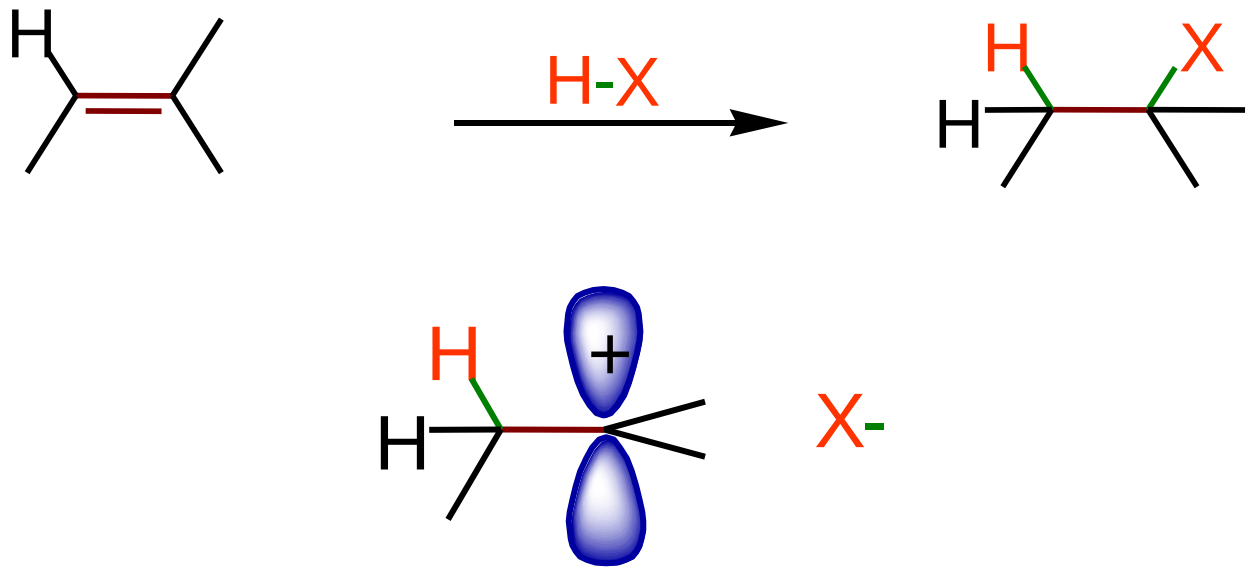
π- bond as nucleophile



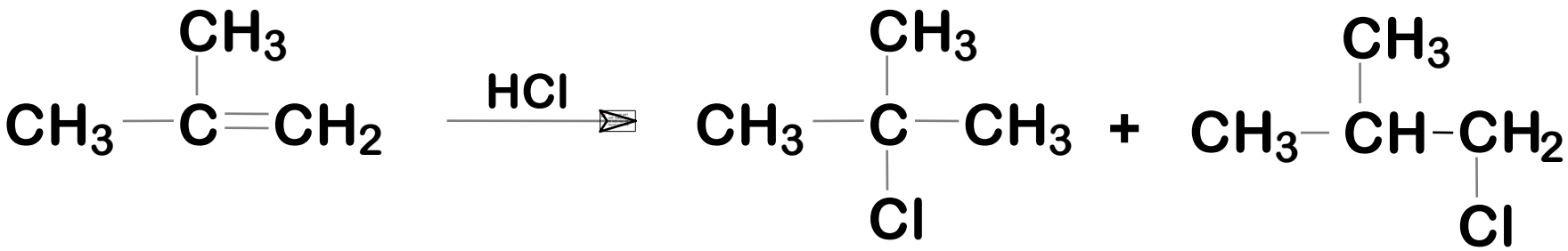
H-Hal addition



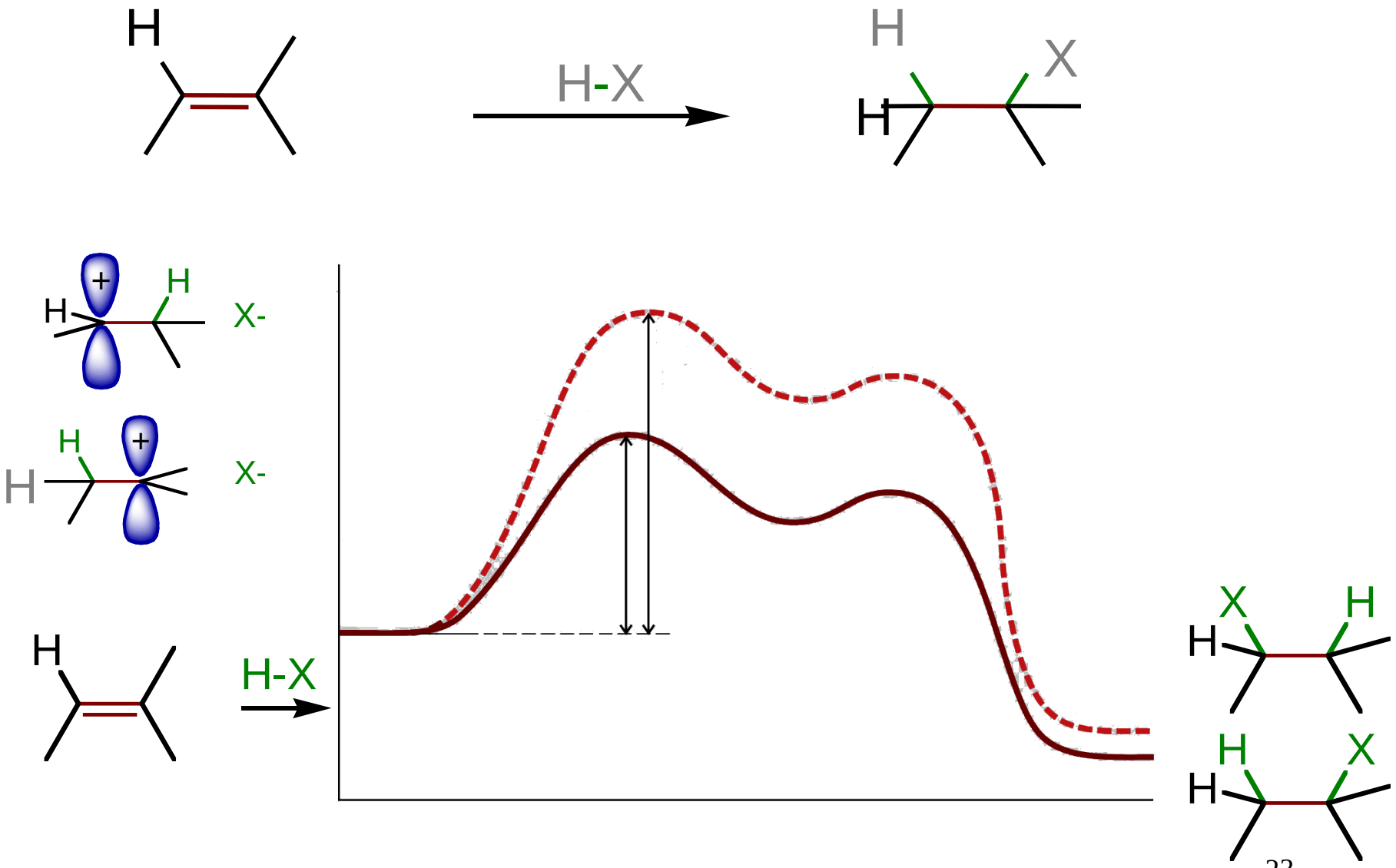
Markovnikov Rule



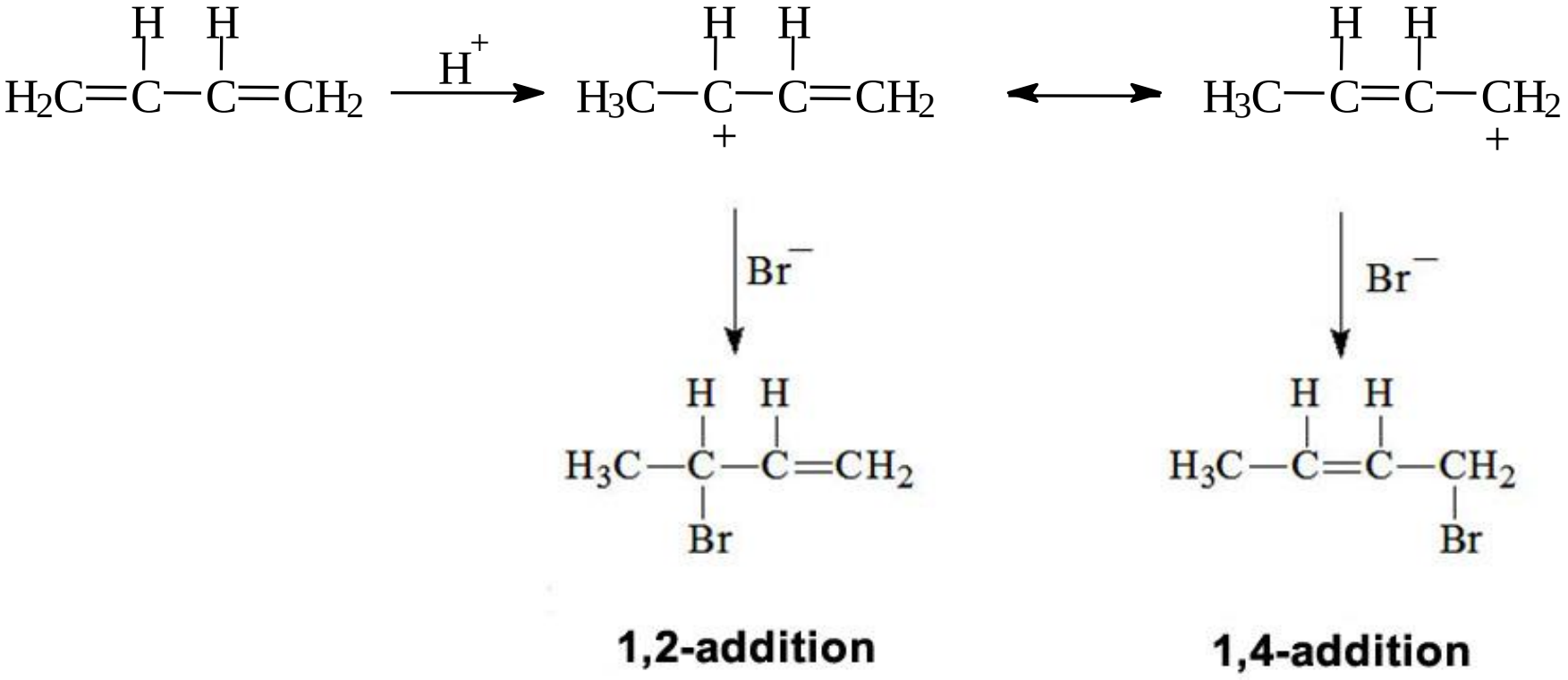
Markovnikov Rule



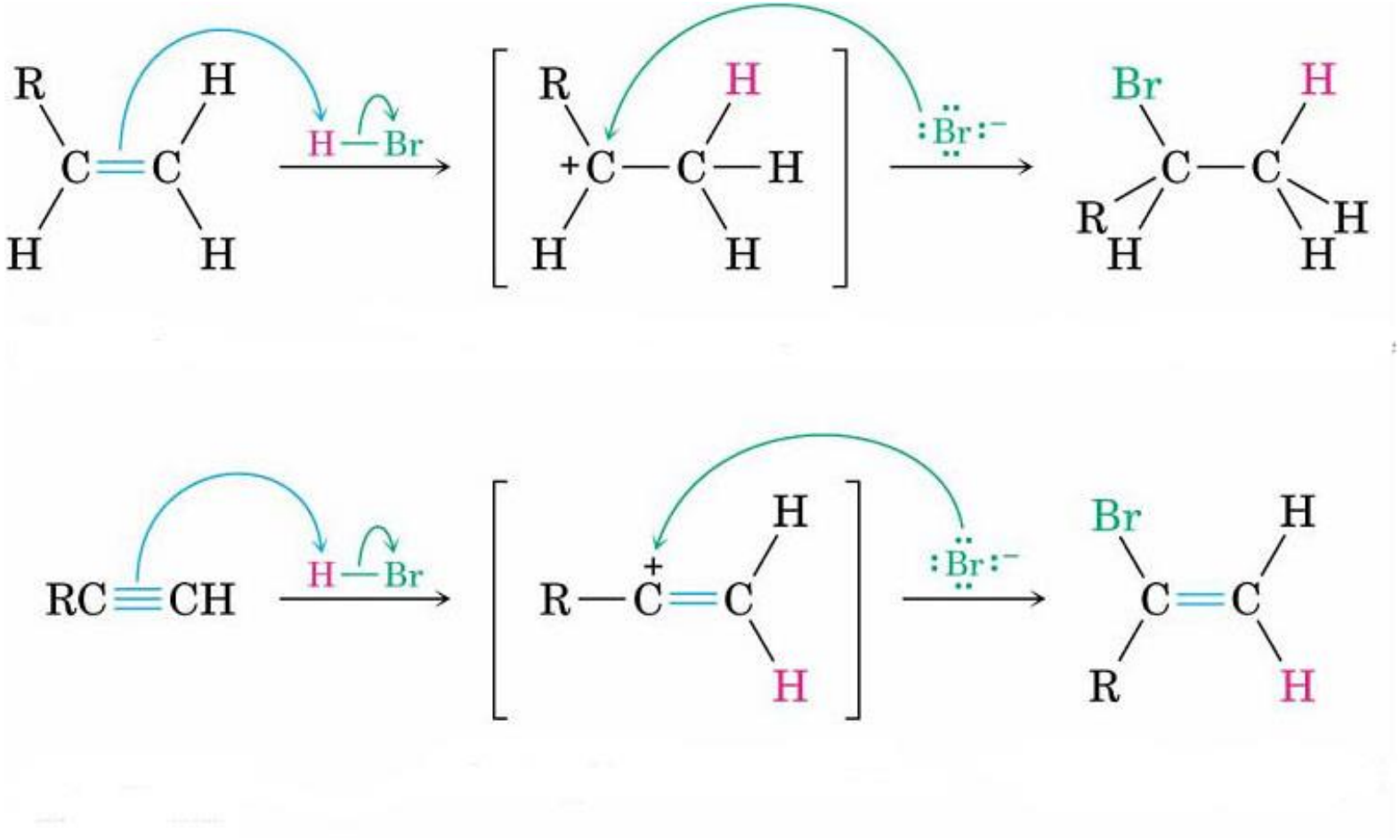
Main product **Side product**


H
H-X
H
X
+
H
H
X-
H
+
H
H
X-
H
H-X
X
H
H
H
X

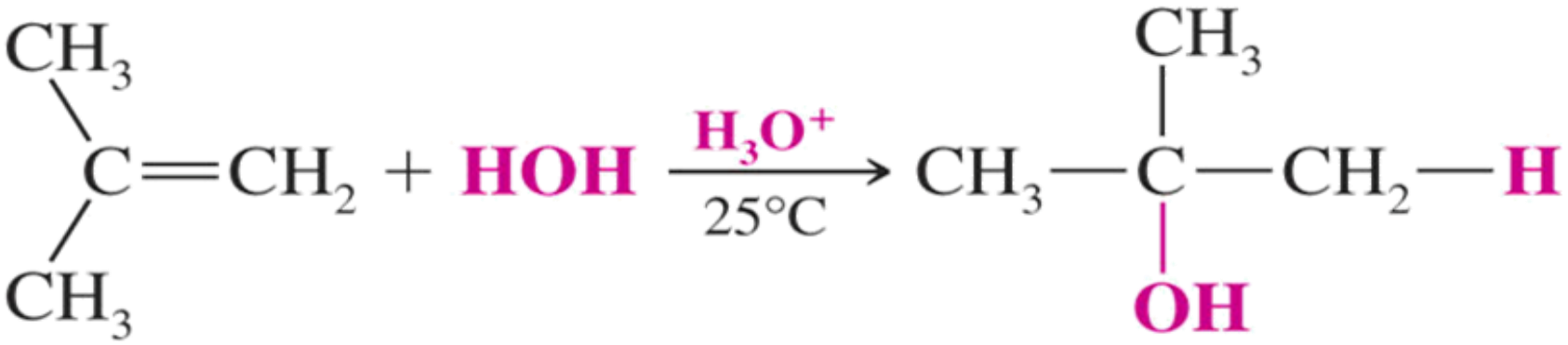
Conjugated double bonds

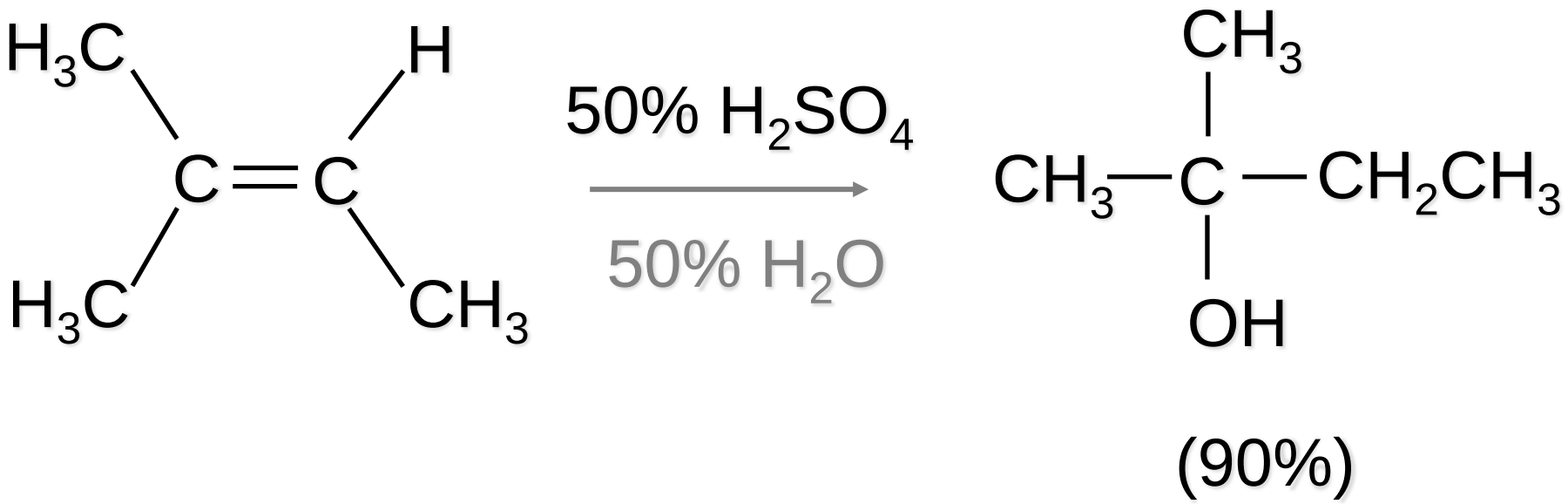


Triple bonds

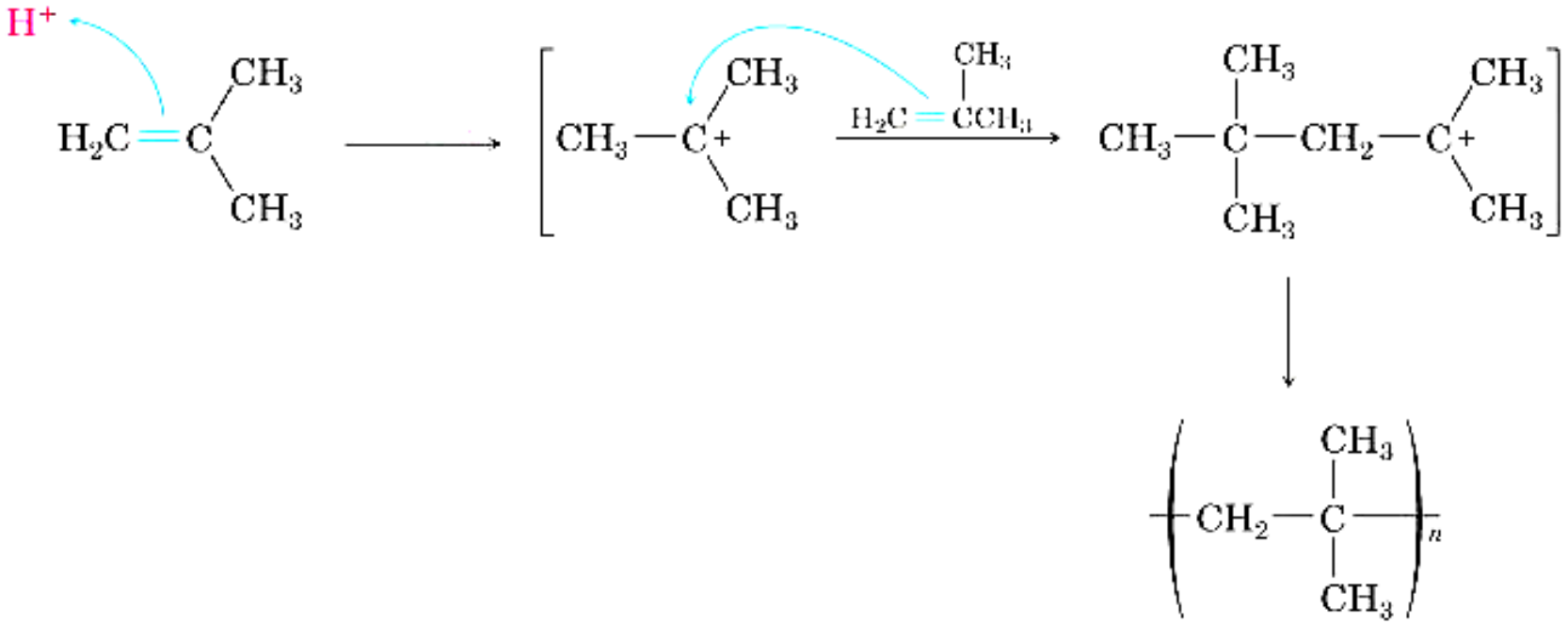


Water addition in acidic medium

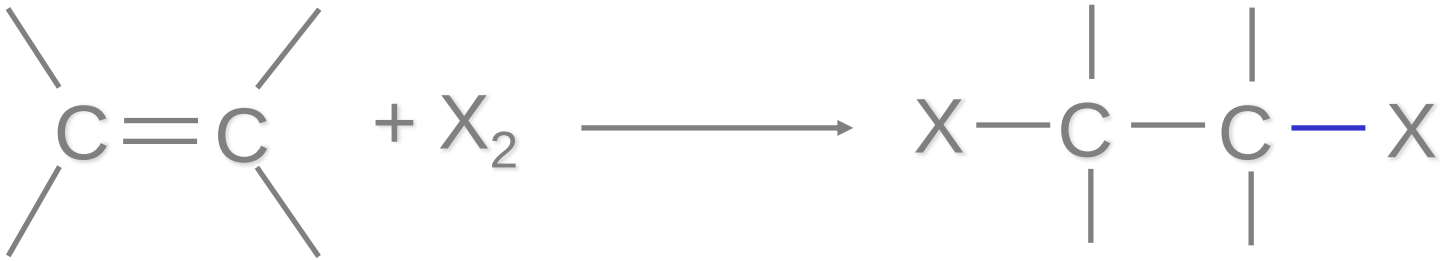


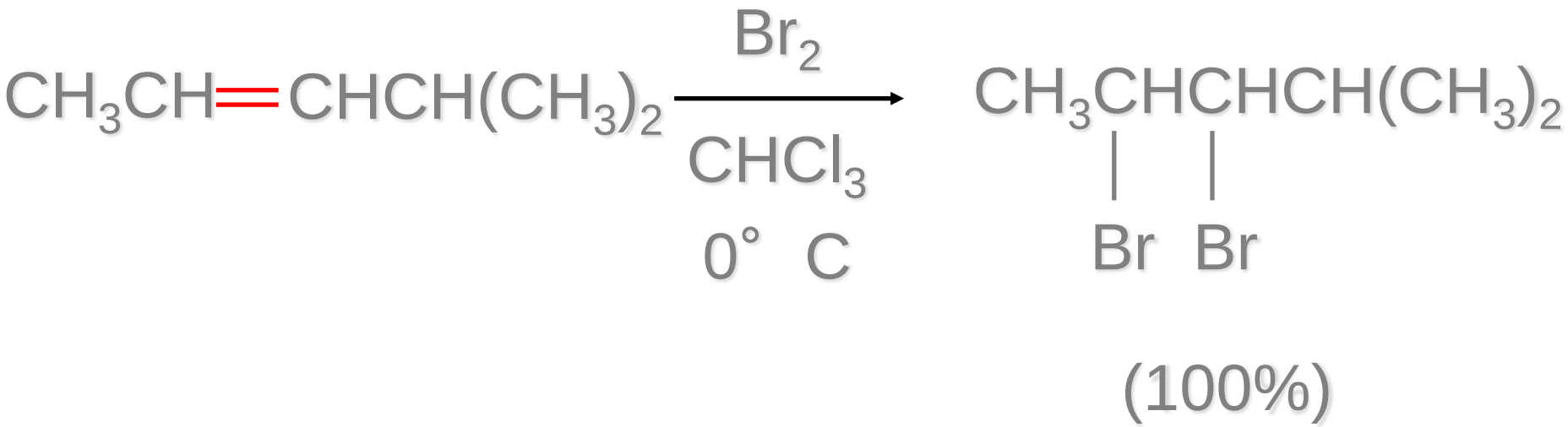

H3C
H
C
C
H3C
CH3
50% H2SO4
50% H2O
CH3
CH3
C
CH2CH3
OH
(90%)

Polymerization

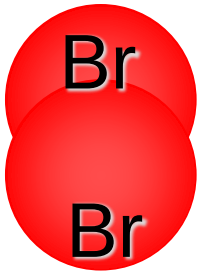


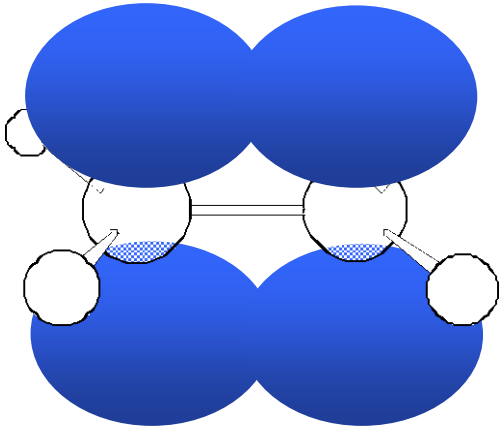
Halogen addition

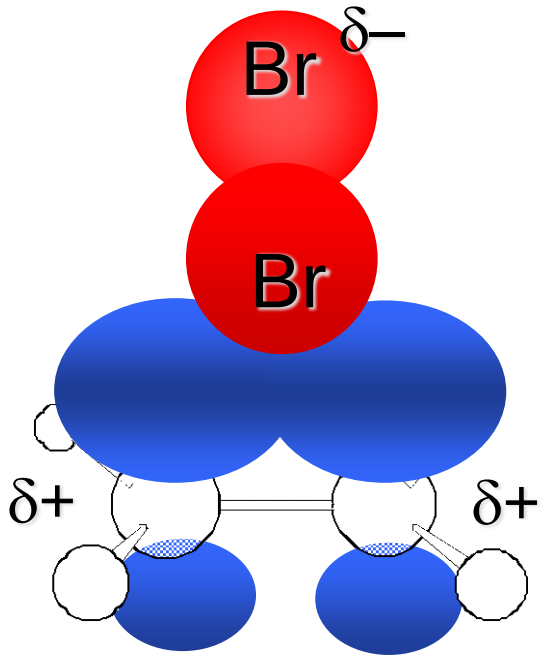


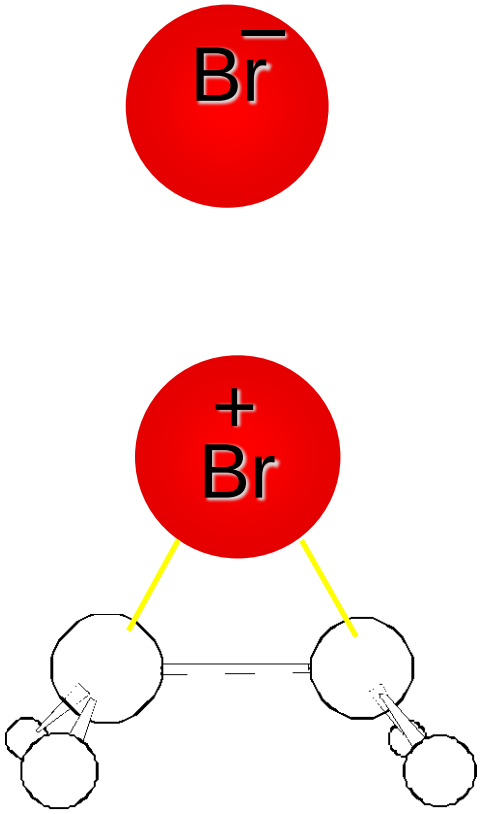


(100%)

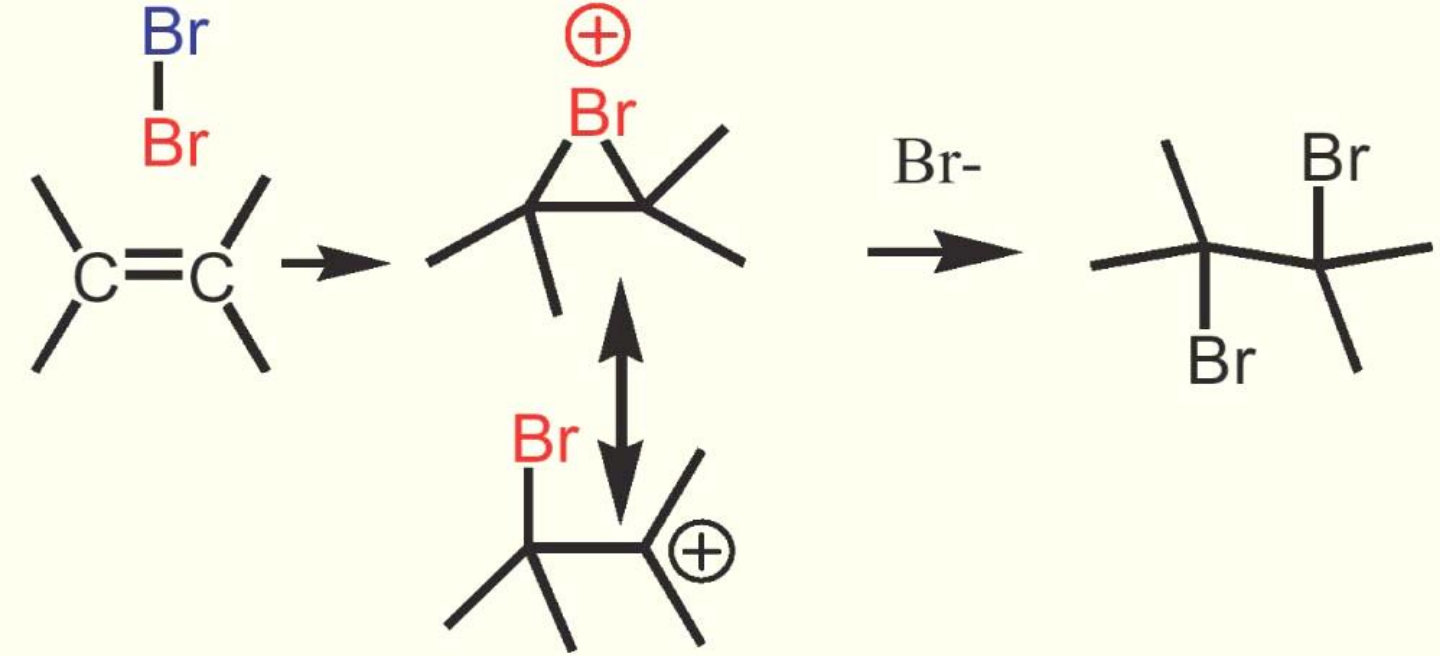

Br
Br

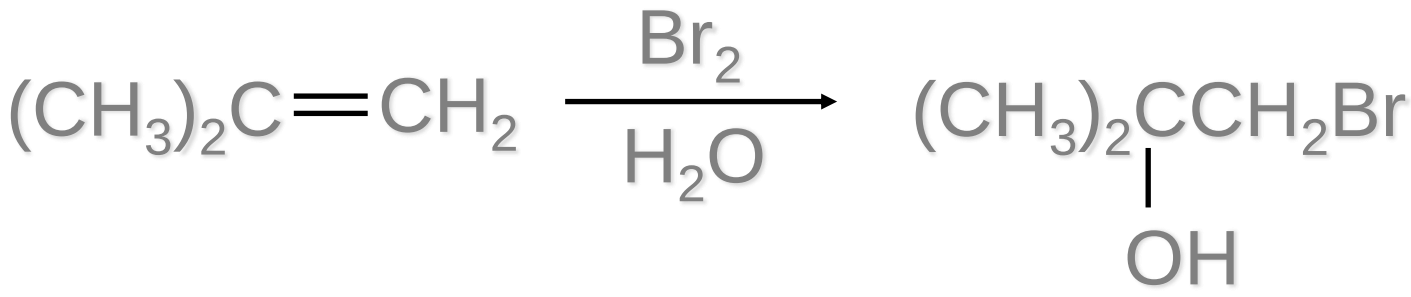



Br
δ–
Br
δ+
δ+


Br
−
+
Br

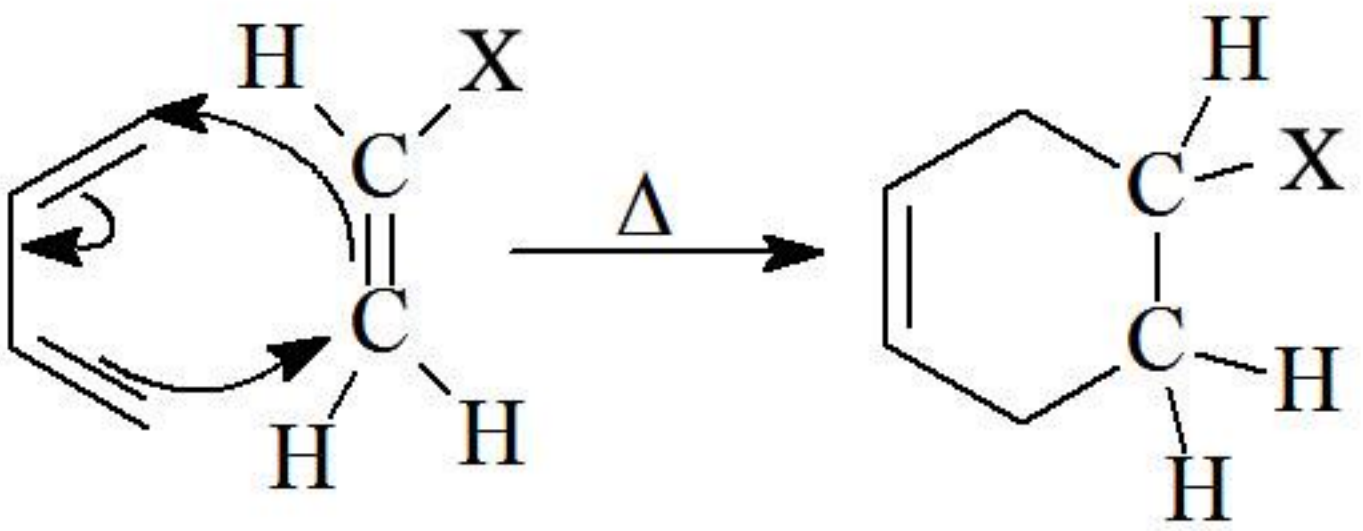
Bromonium ion




(CH3)2C=CH2
Br2
H2O
(CH3)2CCH2Br
OH

Diels-Alderi reaktsioon

- Otto Diels, Kurt Alder; Nobel prize, 1950
- Dieen + alkeen (alküün)



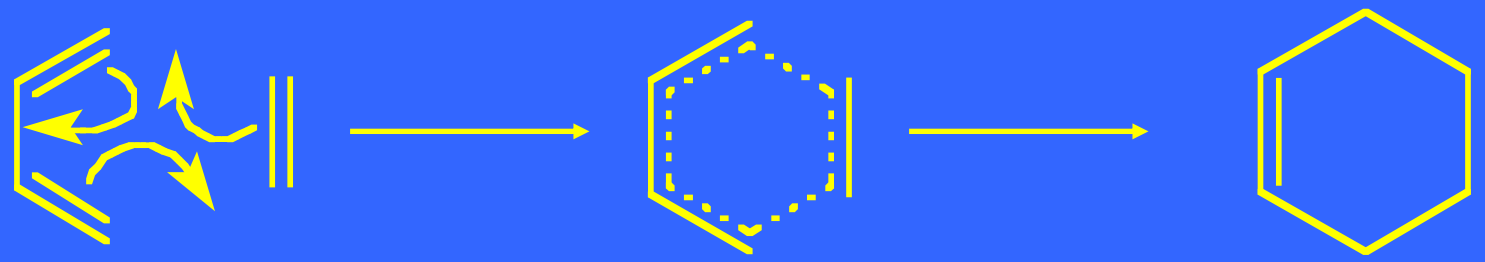
Otto Paul Hermann Diels

1876-1954

Kurt Alder

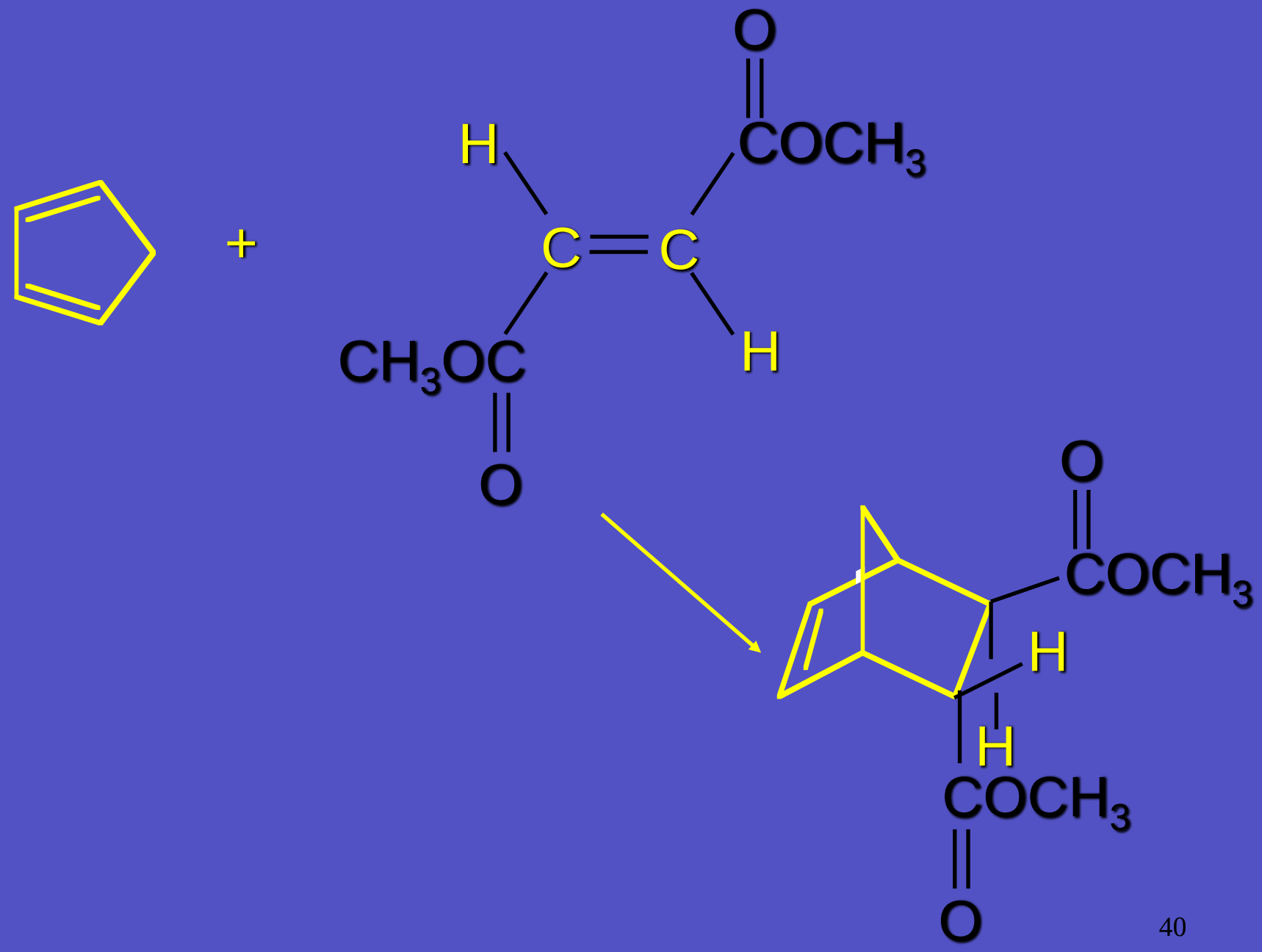
1902-1958

Dien Alkene, Dienophile Cyclohexene



TS

Cyclic reaction


+
O
COCH3
H
C
C
H
CH3OC
O
O
COCH3
H
H
COCH3
O