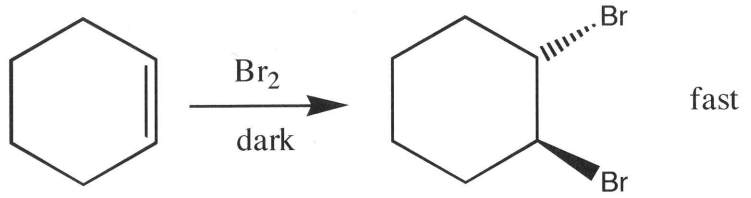
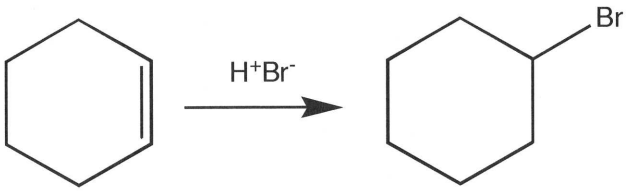
Why Important? Recall Addition Reactions of Alkenes

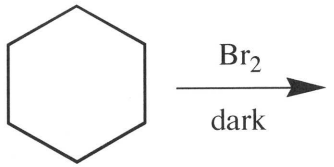
Addition reaction examples



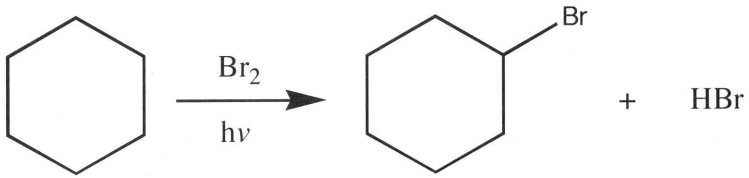
fast



Substitution (slow)

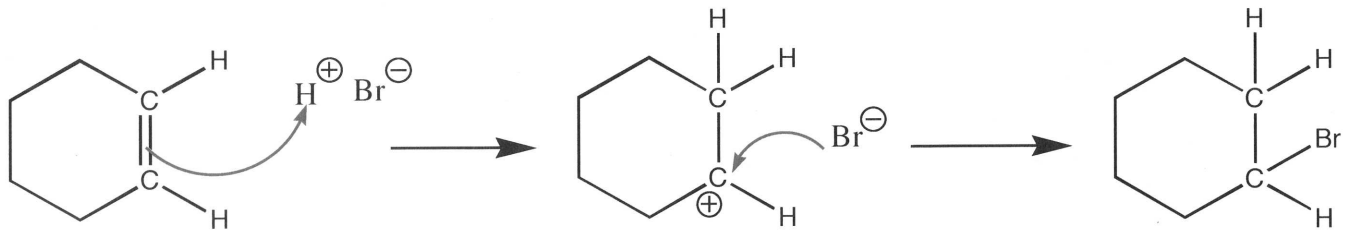


No rxn



+ HBr

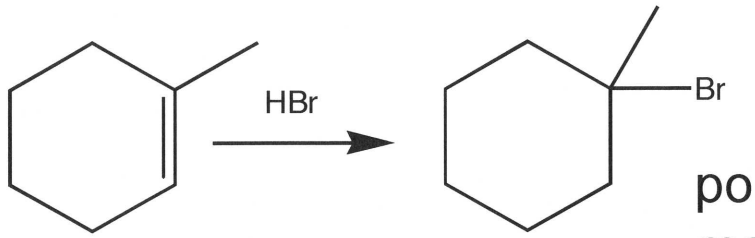
Mechanism



Carbocation intermediate

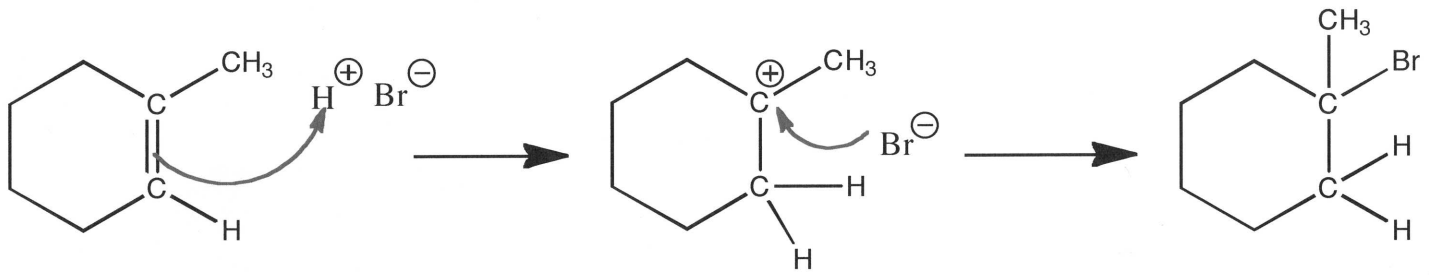
not conjugated cation

Markovnikov Rule for Addition Reactions of Alkenes



1-methylcyclohexene

positive end adds to least substituted side
most stable carbocation intermediate (tertiary)

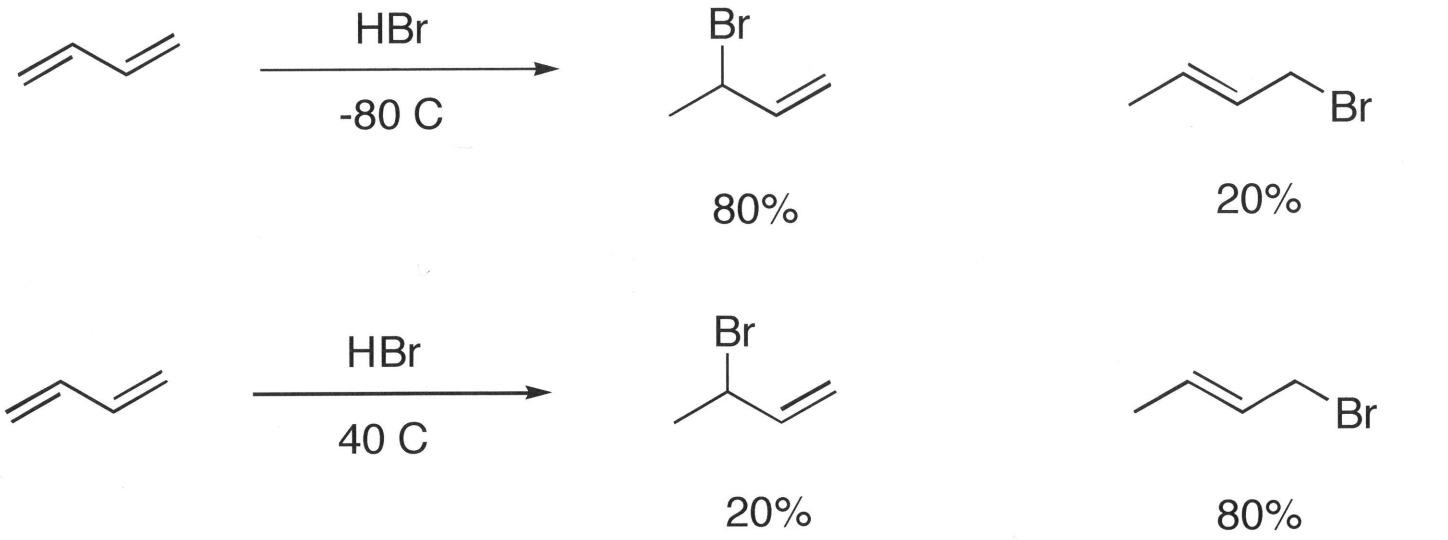


the 3° carbocation is the most stable,
it has more groups stabilizing
the postive charge

cation (and radical) stability: 3° > 2° > 1°

allylic cation > 3° > 2° > 1°

Addition Reactions of Conjugated Systems

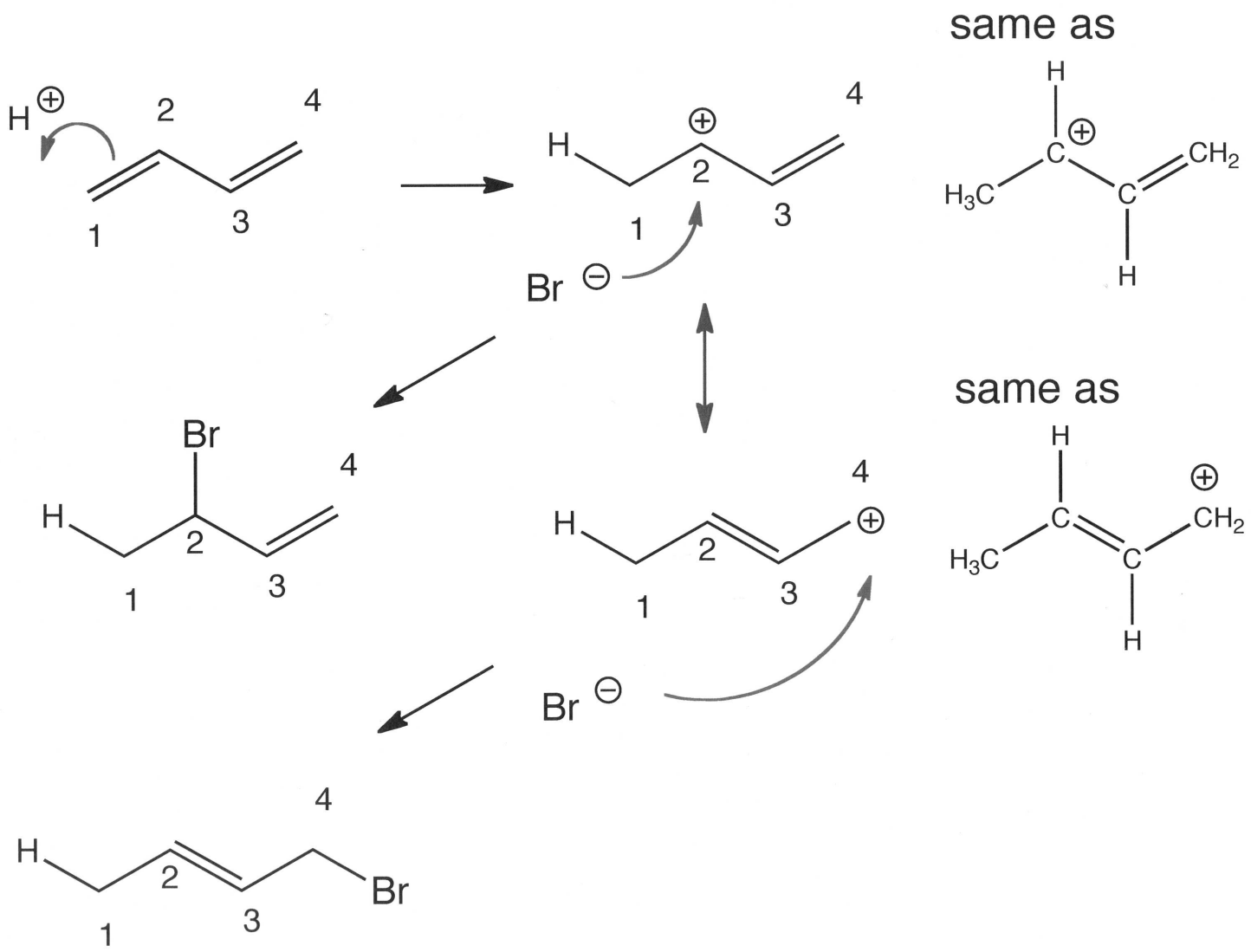


3-bromo-1-butene 1-bromo-2-butene

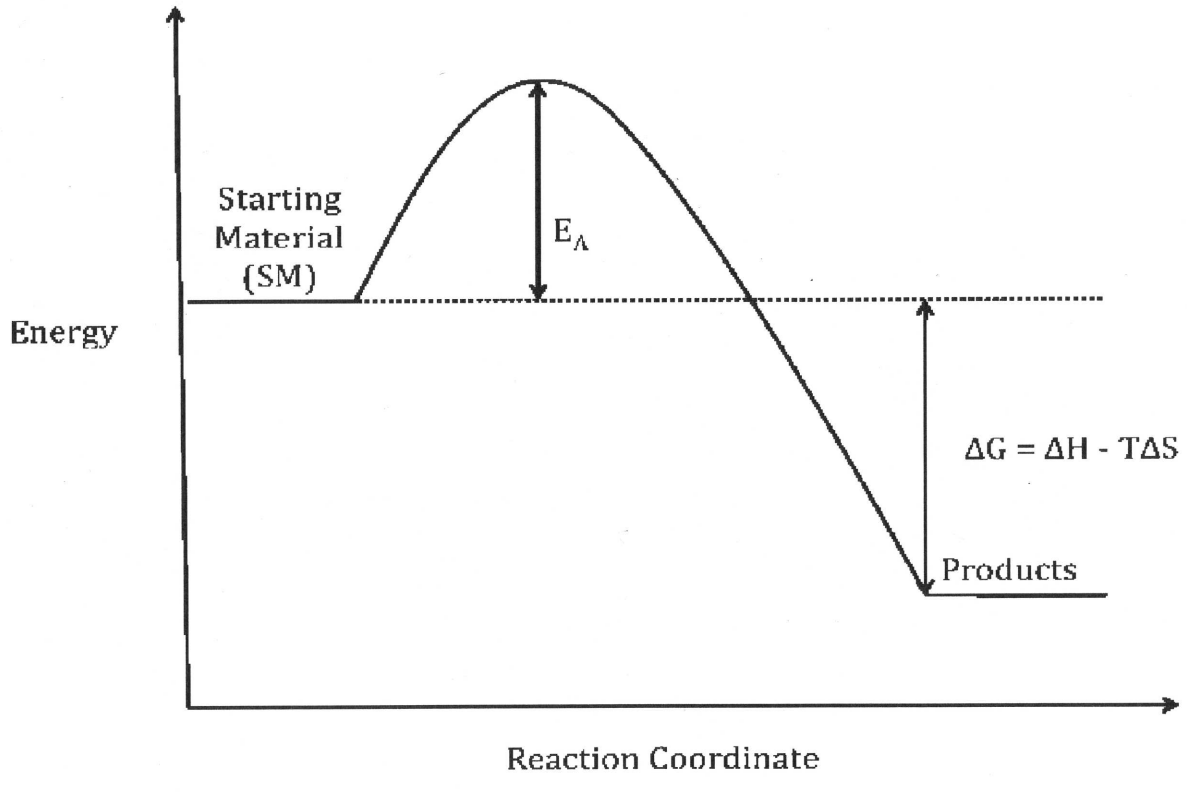
3-bromobutene is a **1,2-addition** product
1-bromo-2-butene is the product of an **1,4-addition** reaction

Why does the temperature affect the ratio obtained ?

Mechanism of Addition to Conjugated System



Energy Diagram : for simple exothermic reaction



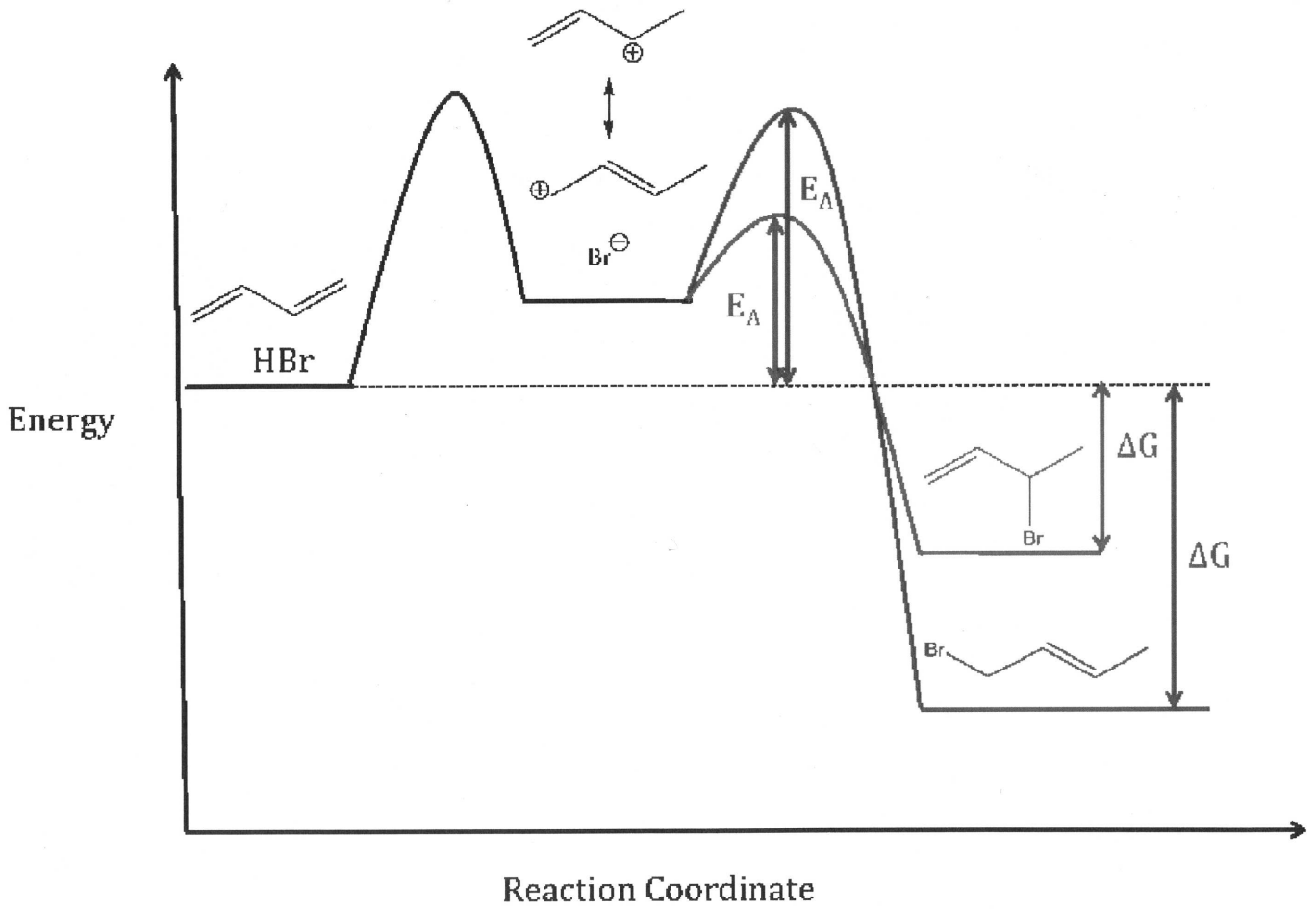
ΔG = free energy of the reaction – this determines ratio of starting material & product

ΔH = enthalpy of the reaction T = temperature in (degrees) Kelvin ΔS = entropy

ΔG determines ratio at equilibrium

E_A = activation energy - determines rate of reaction - how fast - Kinetics

Energy Diagram : for conjugated addition reaction



the activation energy barrier to form the 1,2-product 3-bromo-1-butene
is much *smaller* than the 1,4-product 1-bromo-2-butene; forms fast: kinetic control

However, the energy of 1-bromo-2-butene (1,4 addition)
is lower than 3-bromobutene, so that it is more stable; thermodynamic control

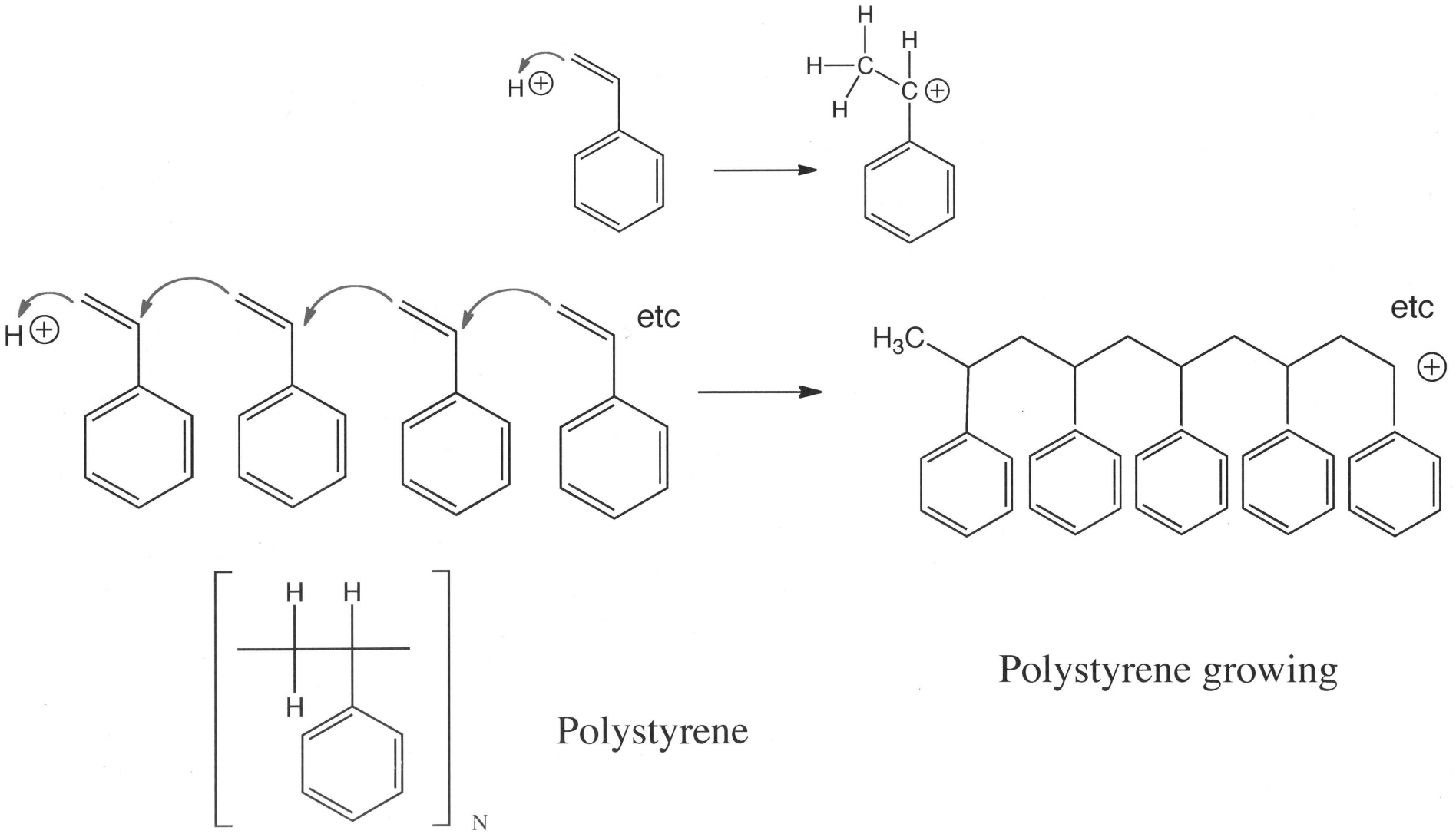
From the 2 resonance forms (connected by the double-sided arrow) of the allylic cation shown in the above figure, we see that the positive charge is shared between the two carbons (C2 and C4) with each carrying a portion of the positive charge.
Note: the allylic cation has two electrons delocalized across the three carbons. It was drawn to have two resonance forms, but it is a ***single entity***, therefore we cannot differentiate and speak of one form being a primary carbocation (therefore less stable) and the other being a secondary carbocation (therefore more stable).

- 3 - bromo-1-butene has a h igher yield at the lower temperature because it is kinetically more favoured. It formed faster than 1-bromo-2-butene. **Kinetic Control**

3-bromo-1-butene has lower yield than 1-bromo-2-butene at higher temperature due to **thermodynamic control**. The addition of bromine to the allylic cation is reversible at high temperature. 3-Bromo-1-butene can be converted back to the allylic cation and then form 1-bromo-2-butene, which is the thermodynamically more favoured product

Practical application for conjugated addition reaction

Example: Polystyrene Synthesis by **Conjugated Cation Process**

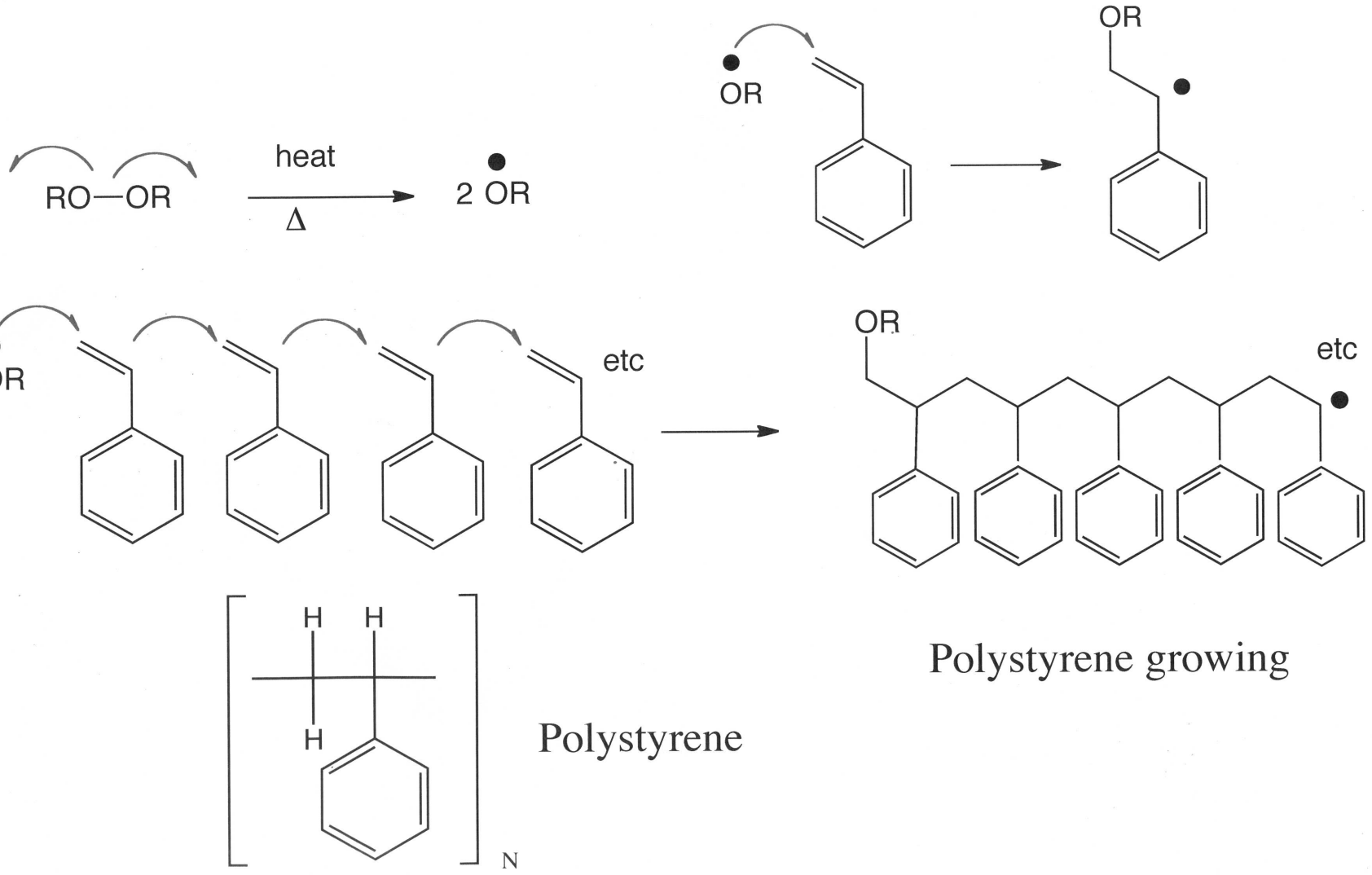


Polystyrene

Polystyrene growing

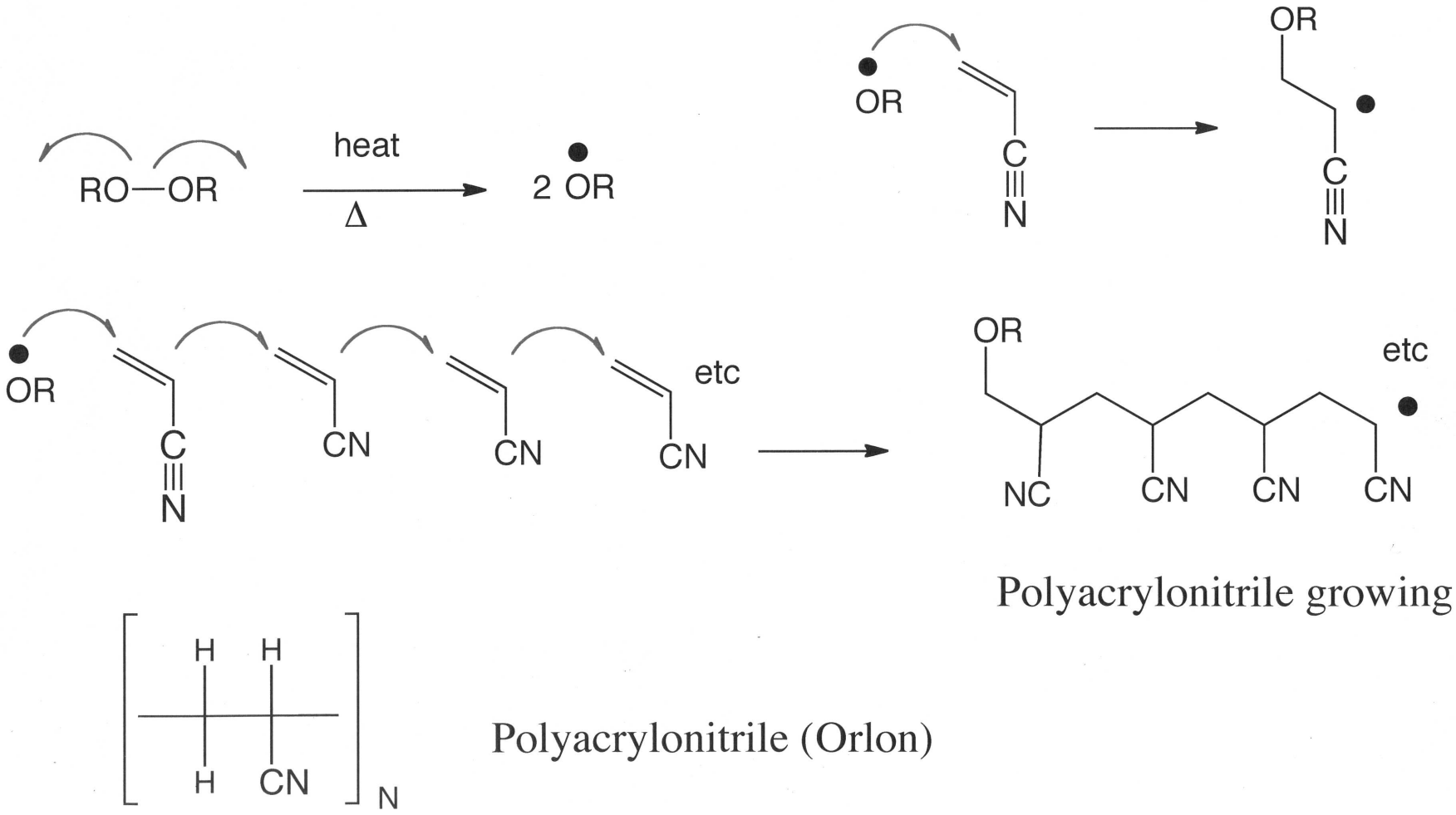
Practical application for conjugated addition reaction

Example: Polystyrene Synthesis by **Conjugated Radical Process**



Practical application for conjugated addition reaction

Example: Polyacrylonitrile (Orlon) Synthesis by **Conjugated Radical Process**



Polyacrylonitrile growing

Polyacrylonitrile (Orlon)