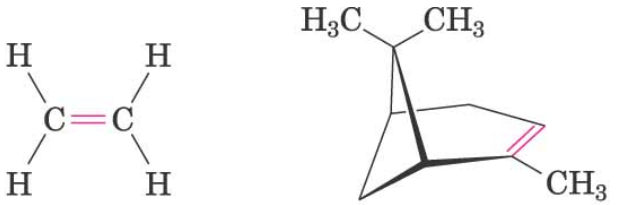
6. Alkenes: Structure and Reactivity

Alkenes - Hydrocarbons With Carbon-Carbon Double Bonds

- Also called an olefins
- Include many naturally occurring materials
  - Flavors, fragrances, vitamins
- Important industrial products
  - These are feed stocks for industrial processes



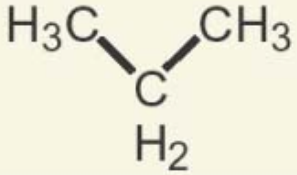
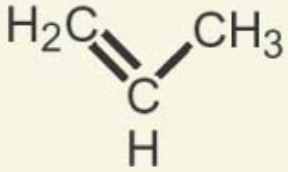
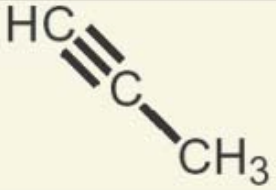
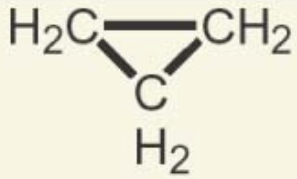
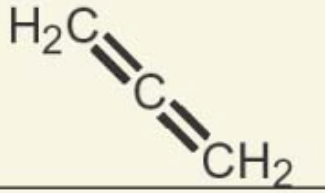
Ethylene

α-Pinene

β-Carotene
(orange pigment and vitamin A precursor)

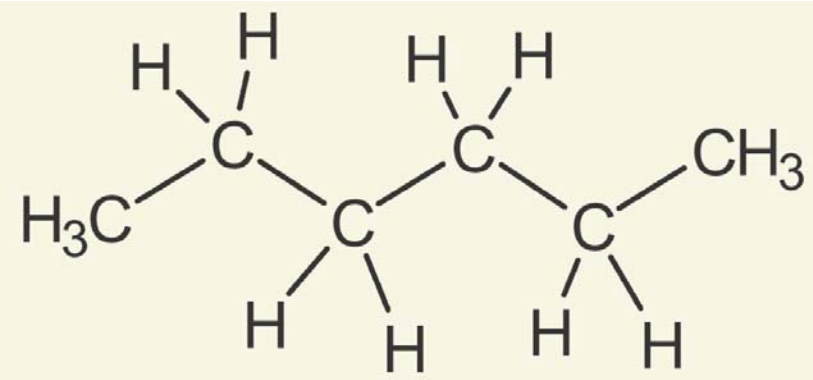
6.2 Degree of Unsaturation

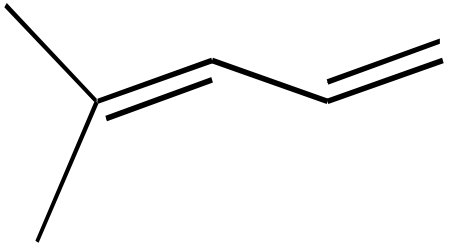
- Relates molecular formula to possible structures
- Degree of unsaturation: number of multiple bonds or rings.
- Remember formula for saturated a acyclic compound is C_nH_{2n+2}
- Each ring or multiple bond replaces 2 H's

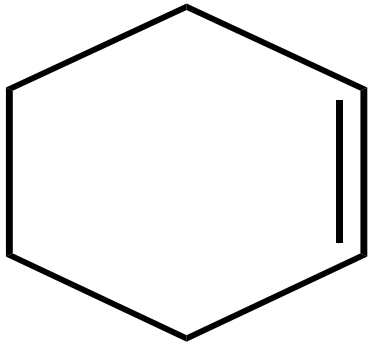
0	1	2
		
		
C_3H_8	C_3H_6	C_3H_4

Example: C_6H_{10}

- Saturated is C_6H_{14}
  - Therefore 4 H's are not present
- Four hydrogens missing is two degrees of unsaturation
  - Two double bonds?
  - Or a triple bond?
  - or two rings
  - or a ring and double bond

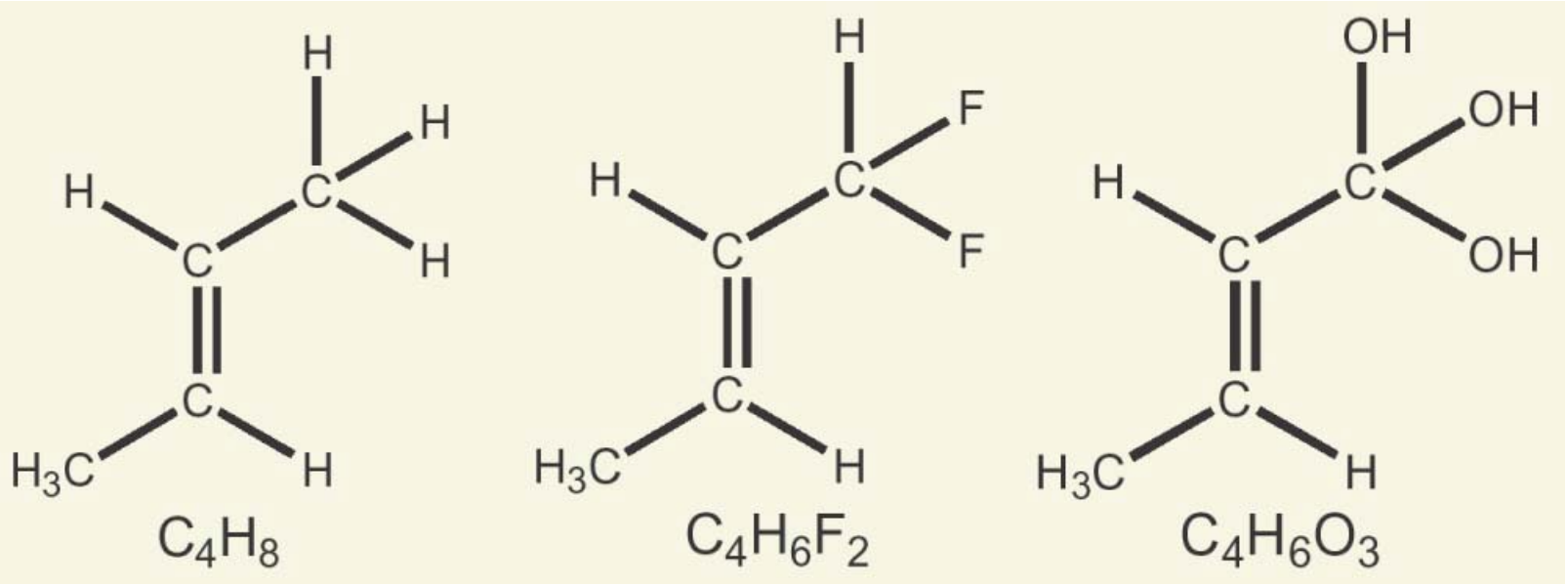






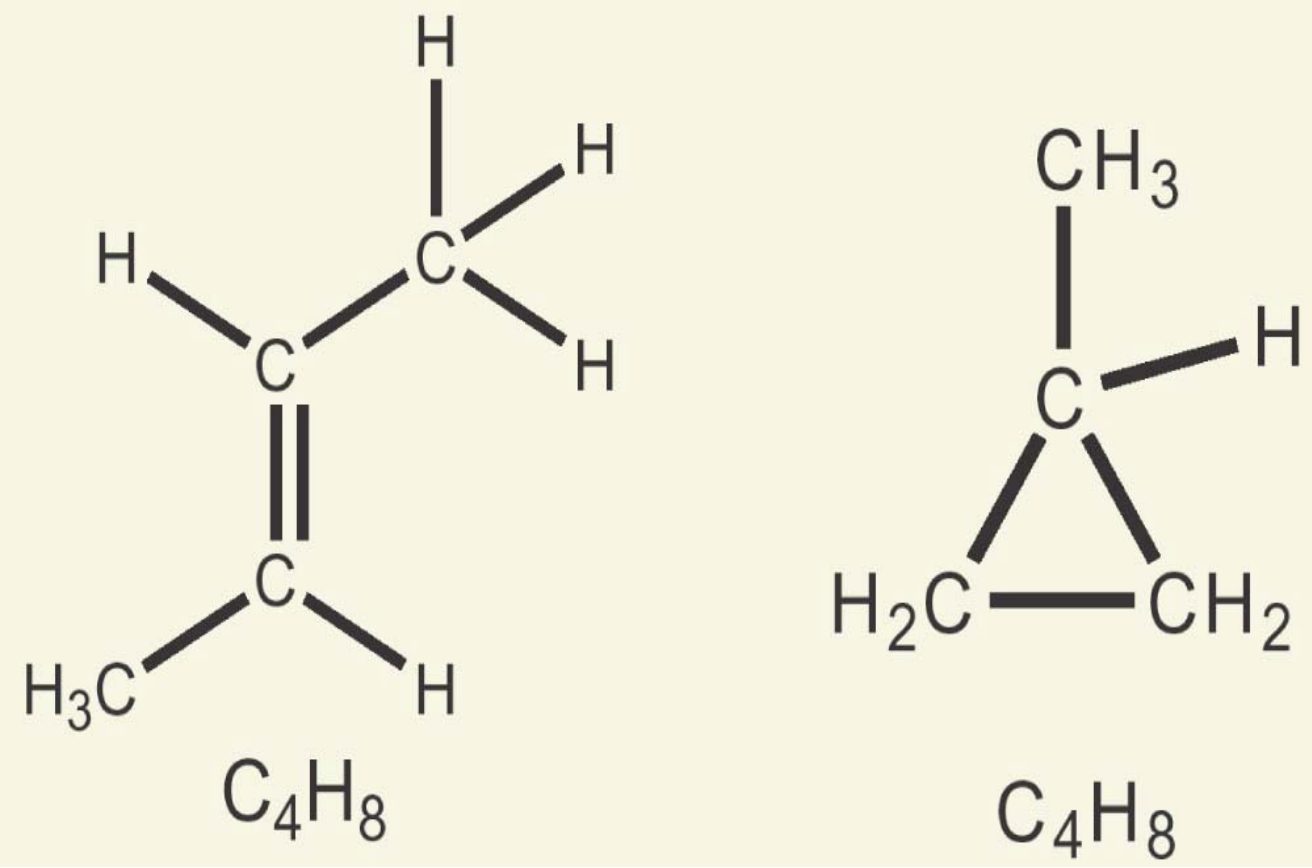
Degree of Unsaturation With Other Elements

- Organohalogens (X: F, Cl, Br, I)
  - Halogen replaces hydrogen
- $C_4H_6Br_2$ and C_4H_8 have one degree of unsaturation
- Oxygen atoms - if connected by single bonds
  - These don't affect the total count of H's



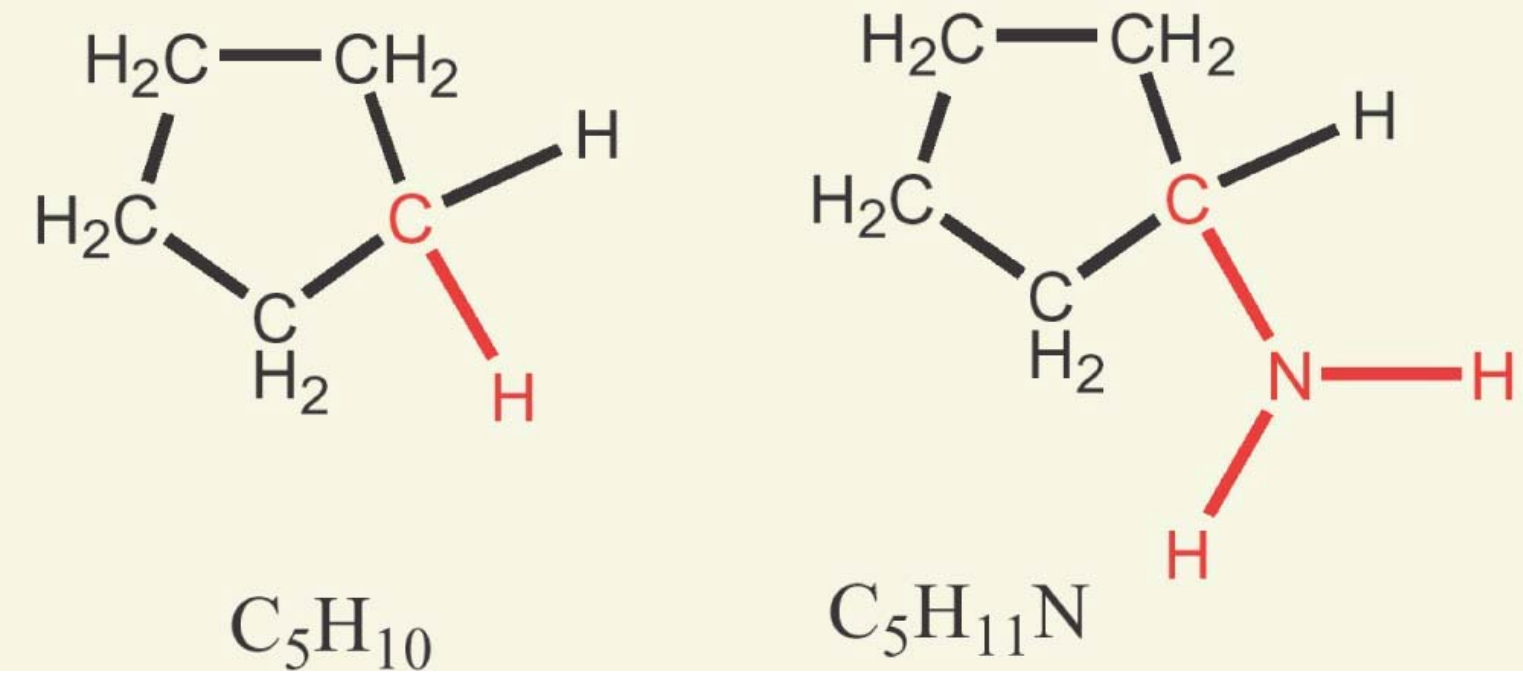
Degree of Unsaturation and Variation

- Compounds with the same degree of unsaturation can have many things in common and still be very different



If C-N Bonds Are Present

- Nitrogen has three bonds
  - So if it connects where H was, it adds a connection point
  - Subtract one H for equivalent degree of unsaturation in hydrocarbon

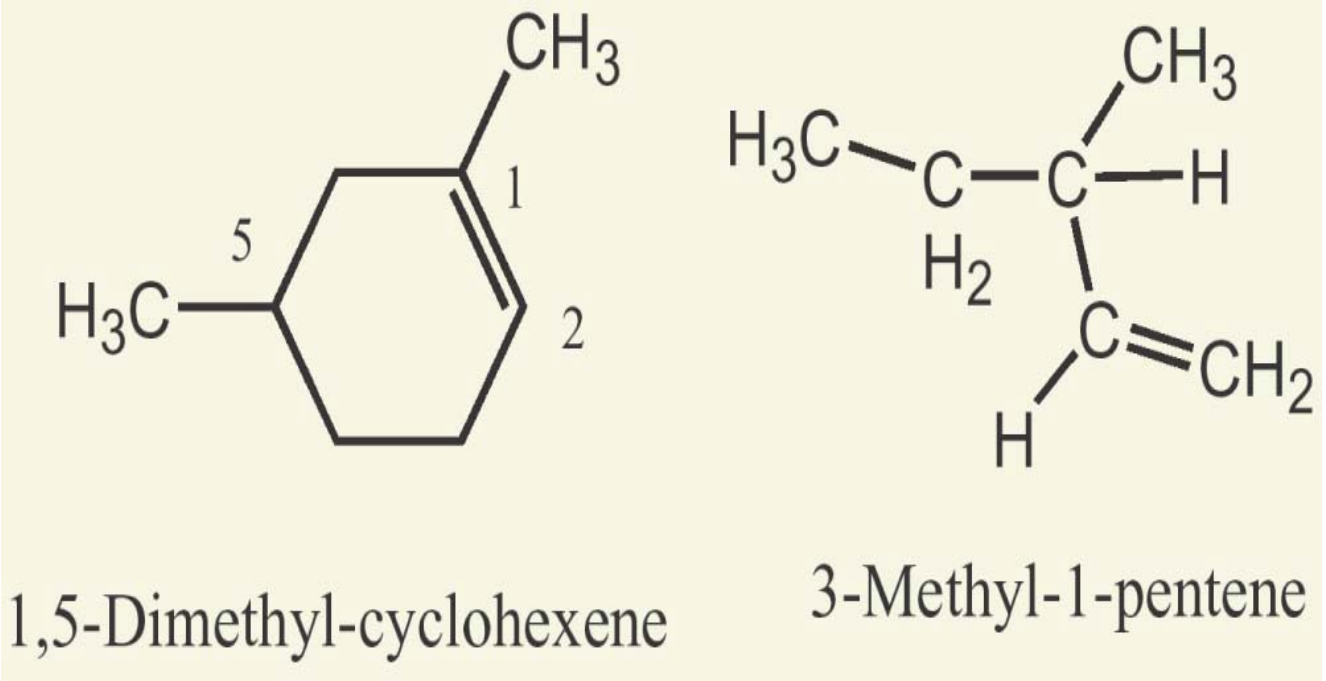


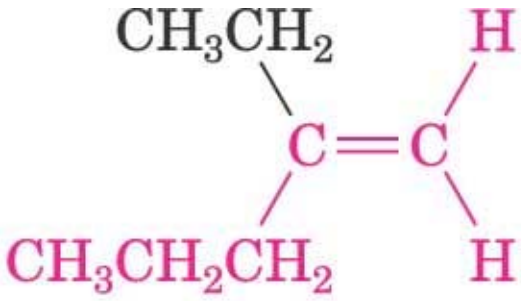
6.3 Naming of Alkenes

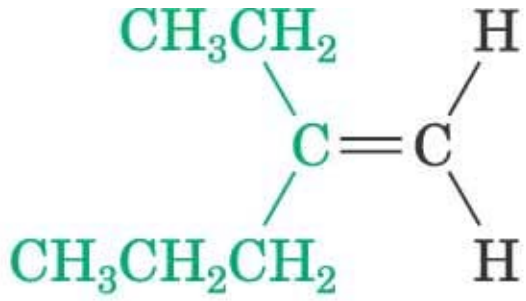
- Find longest continuous carbon chain that contains CC db

for root name, Number carbons in chain so that double bond carbons have lowest possible numbers

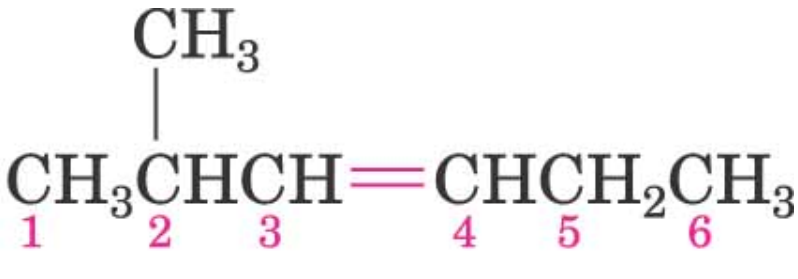
- Rings have “cyclo” prefix



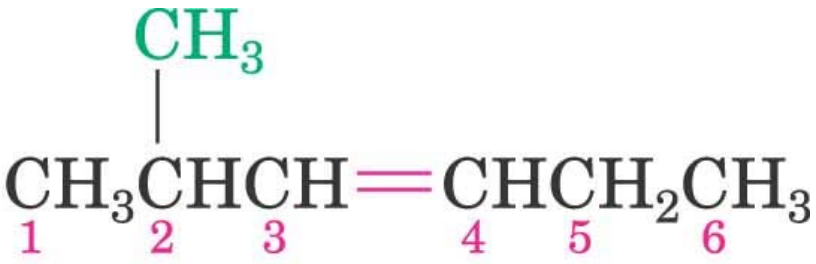




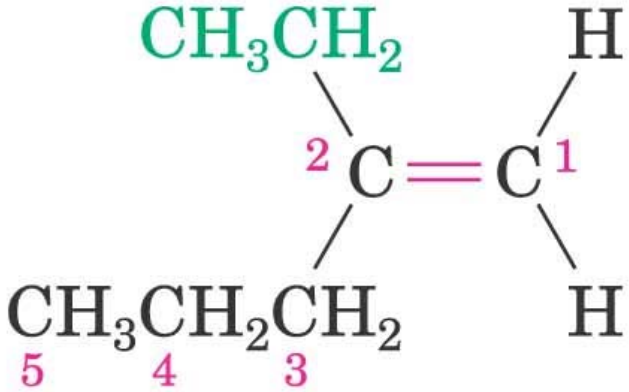
Named as a *pentene* *NOT* as a hexene, since the double bond is not contained in the six-carbon chain



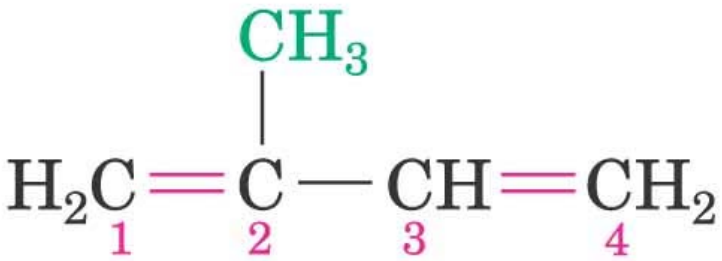
2-Hexene



2-Methyl-3-hexene



2-Ethyl-1-pentene



2-Methyl-1,3-butadiene

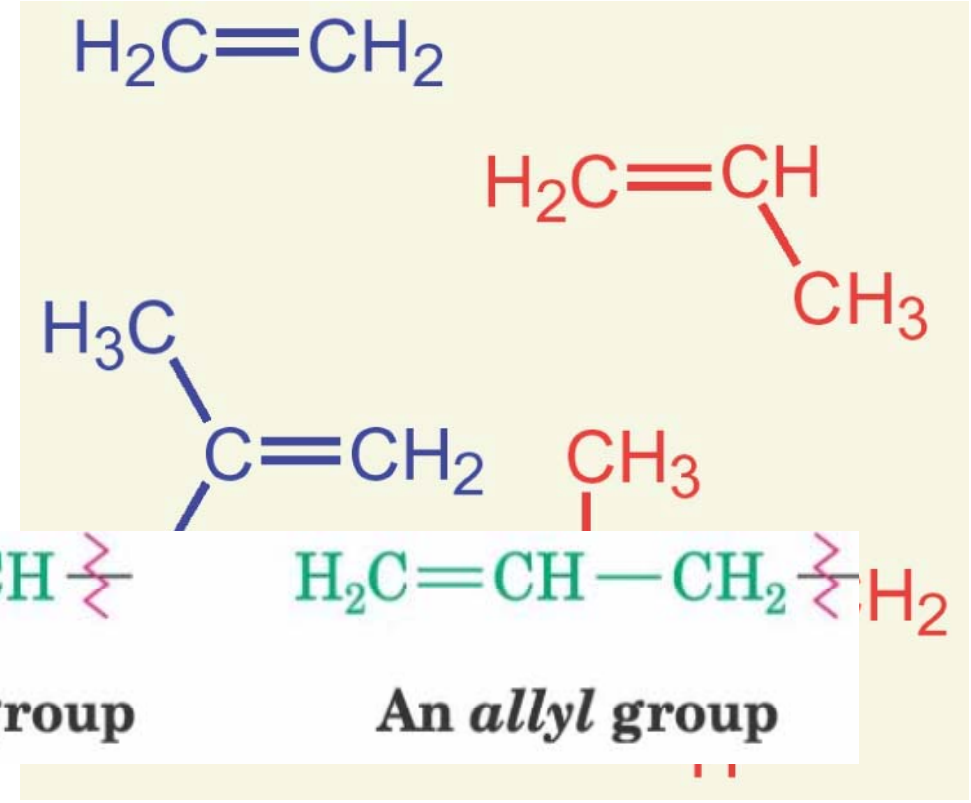
Many Alkenes Are Known by Common Names

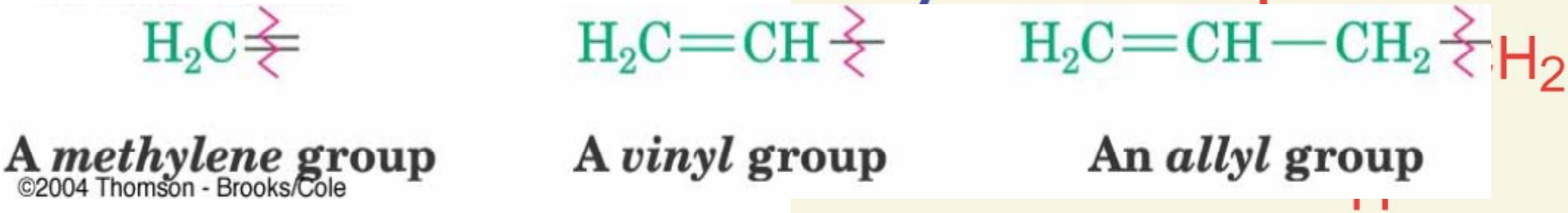
Ethylene = ethane

Propylene = propene

Isobutylene = 2-methylpropene

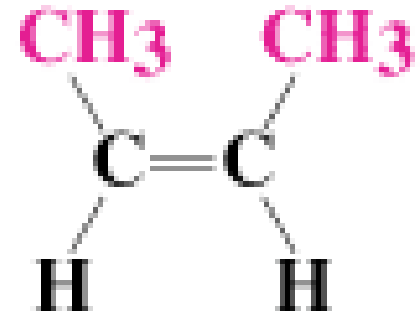
Isoprene = 2-methyl-1,3-butadiene



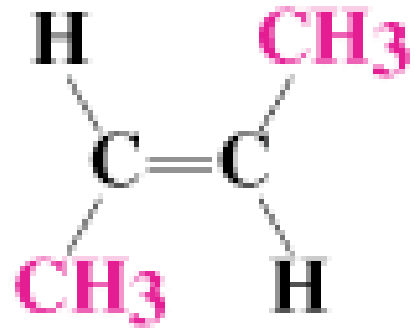


6.5 Cis-Trans Isomerism in Alkenes

- The presence of a carbon-carbon double can create two possible structures
  - *cis* isomer - two similar groups on same side of the double bond
  - *trans* isomer similar groups on opposite sides
- Each carbon must have two different groups for these isomers to occur



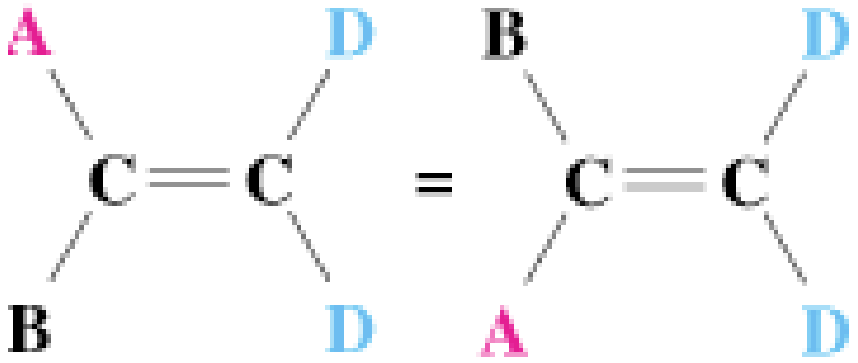
cis-2-Butene



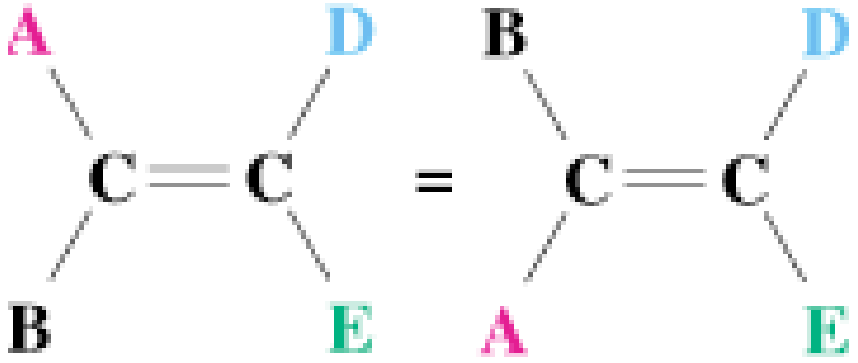
trans-2-Butene

Cis, Trans Isomers Require That End Groups Must Differ in Pairs

- 180°rotation superposes

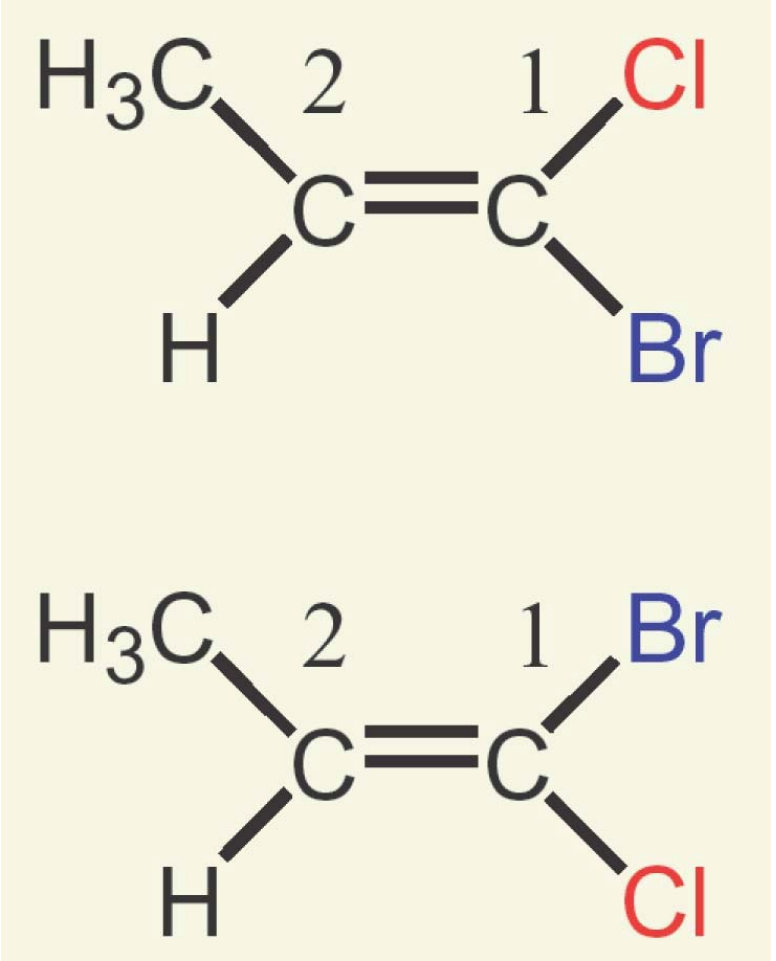


- Bottom pair cannot be superposed without breaking C=C



6.6 Sequence Rules: The *E*, *Z* Designation

- Neither compound is clearly "*cis*" or "*trans*"
  - Substituents on C1 are different than those on C2
  - We need to define "similarity" in a precise way to distinguish the two stereoisomers
- *Cis*, *trans* nomenclature only works for disubstituted double bonds (2 Hs and 2 other groups)



A System for Comparison of Substituent Priority (Ranking Priorities: Cahn-Ingold-Prelog Rules)

Rule 1: Must rank atoms that are connected at comparison point
Higher <u>atomic number</u> gets higher priority
In this case,The higher priority groups are *opposite*:

35 17 8 7 6 1
Br > Cl > O > N > C > H

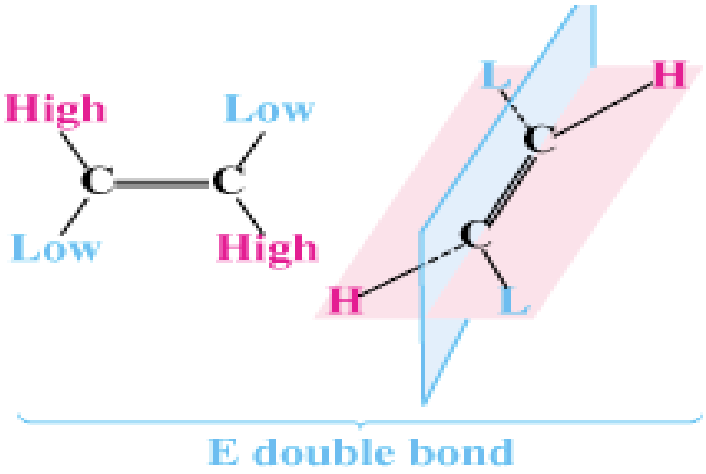
(a) (*E*)-2-Chloro-2-butene **(b) (*Z*)-2-Chloro-2-butene**

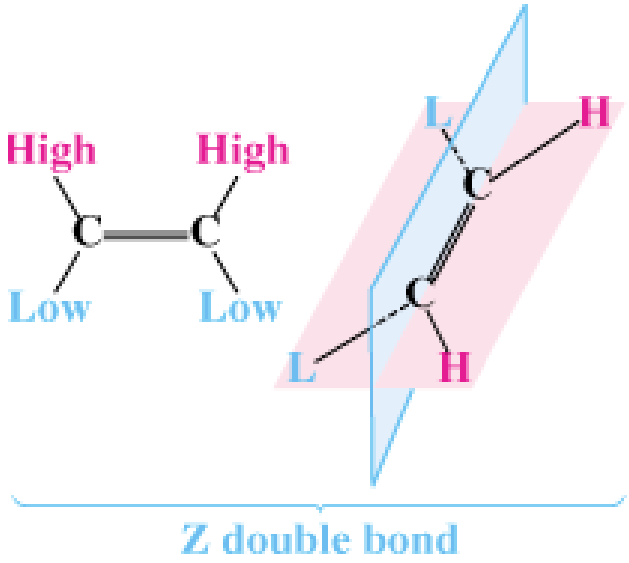
E,Z Stereochemical Nomenclature

- Priority rules of Cahn, Ingold, and Prelog

- Compare where higher priority group is with respect to double bond and designate as prefix

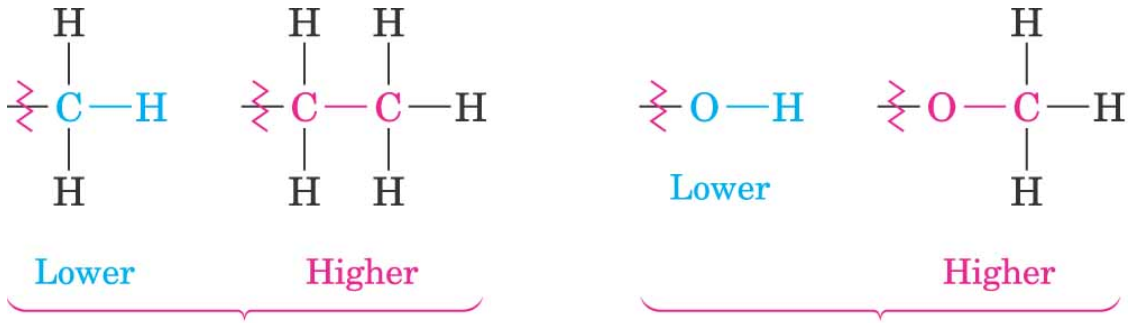
- E -*entgegen*, opposite sides
- Z - *zusammen*, together on the same side

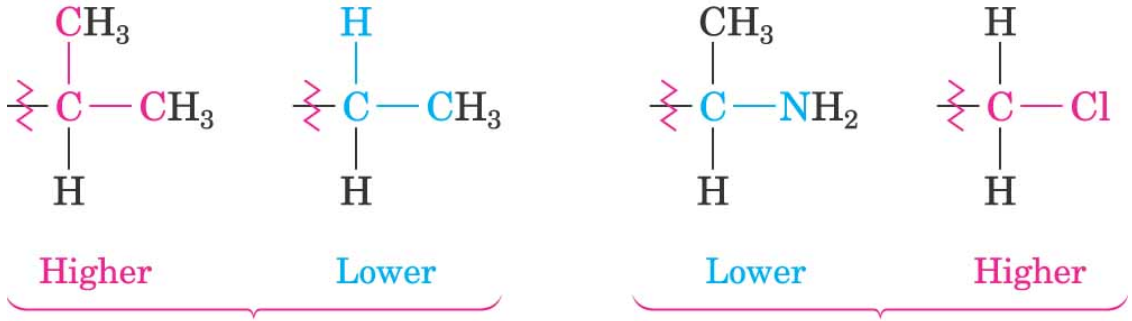




Rule 2: Extended Comparison

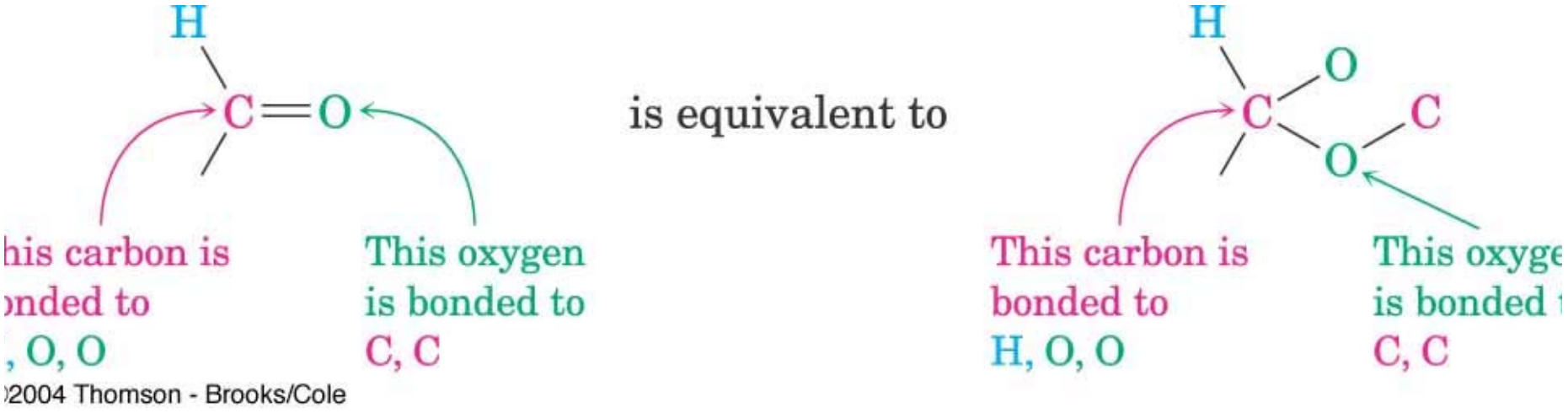
- If atomic numbers are the same at the first connection point, compare at next connection point at same distance
- Compare until something has higher atomic number
- Do not combine – always compare

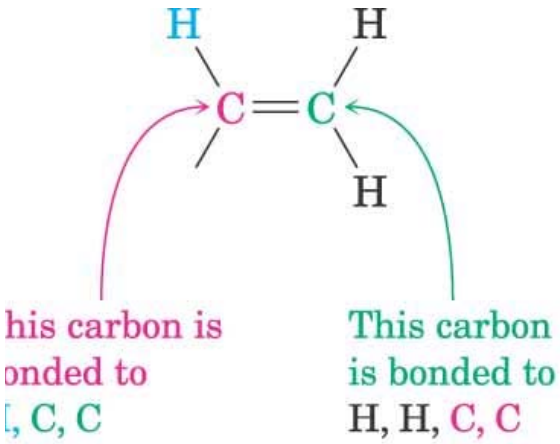




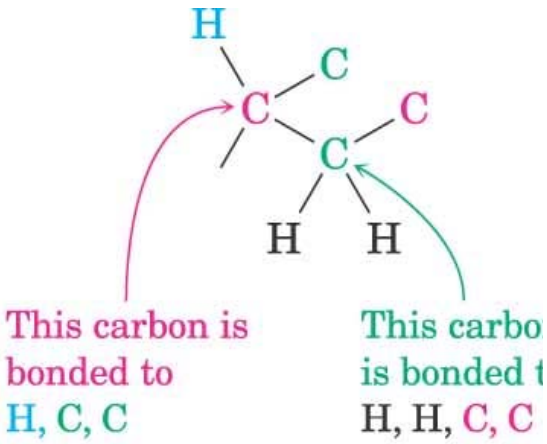
Rule 3: Dealing With Multiple Bonds

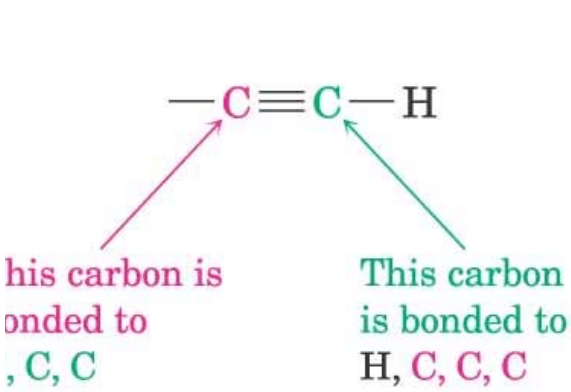
- Substituent is drawn with connections shown and no double or triple bonds. A carbon bonded to an oxygen with a db is considered as a carbon bonded to an oxygen which in turn is bonded to a carbon, all via sb.



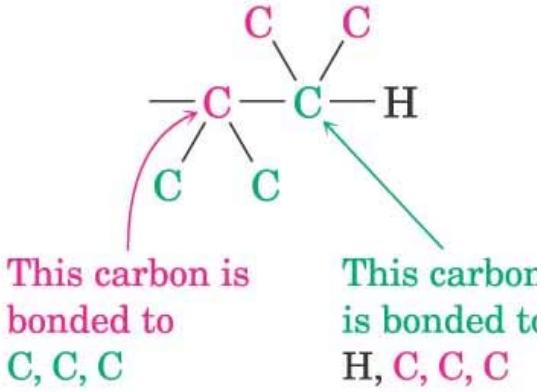


is equivalent to



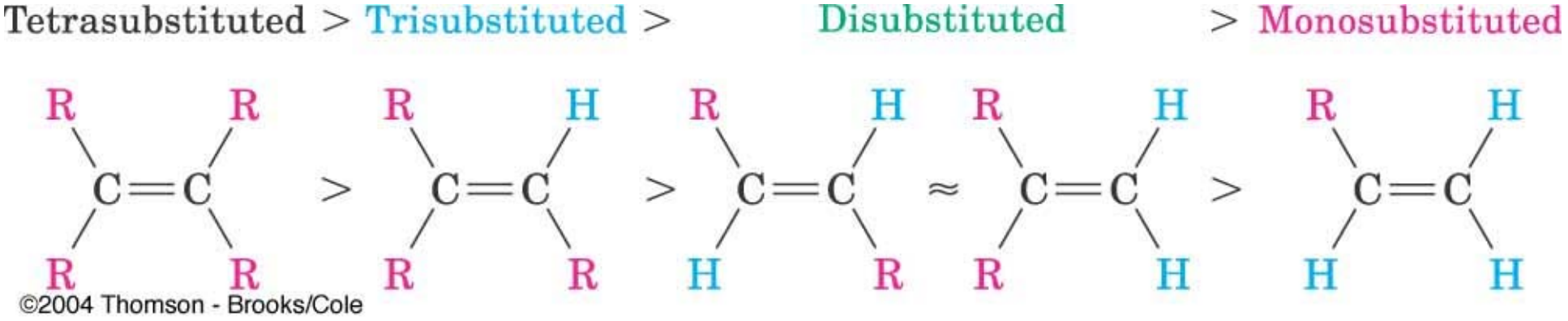


is equivalent to



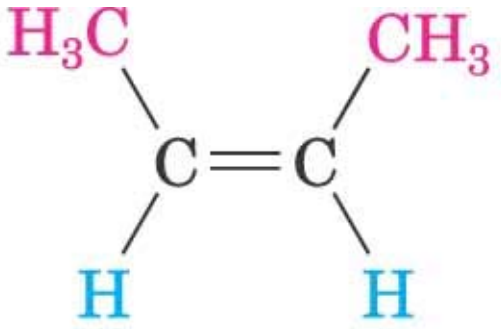
6.7 Alkene Stability

- Cis alkenes are less stable than trans alkenes (why?)
- Compare heat given off on hydrogenation: ΔH^o
- Less stable isomer is higher in energy
  - And gives off more heat
- More highly susbstituted alkenes are more stable
  - Tetrasubstituted (more stable than) > trisubstituted > disubstituted > monosusbtituted



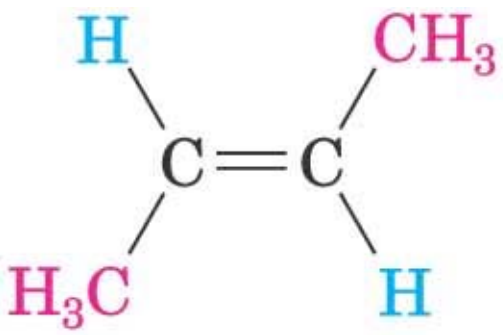
Comparing Stabilities of Alkenes

- Evaluate heat given off when C=C is converted to C-C
- More stable alkene gives off less heat
  - Trans butene generates 5 kJ less heat than cis-butene



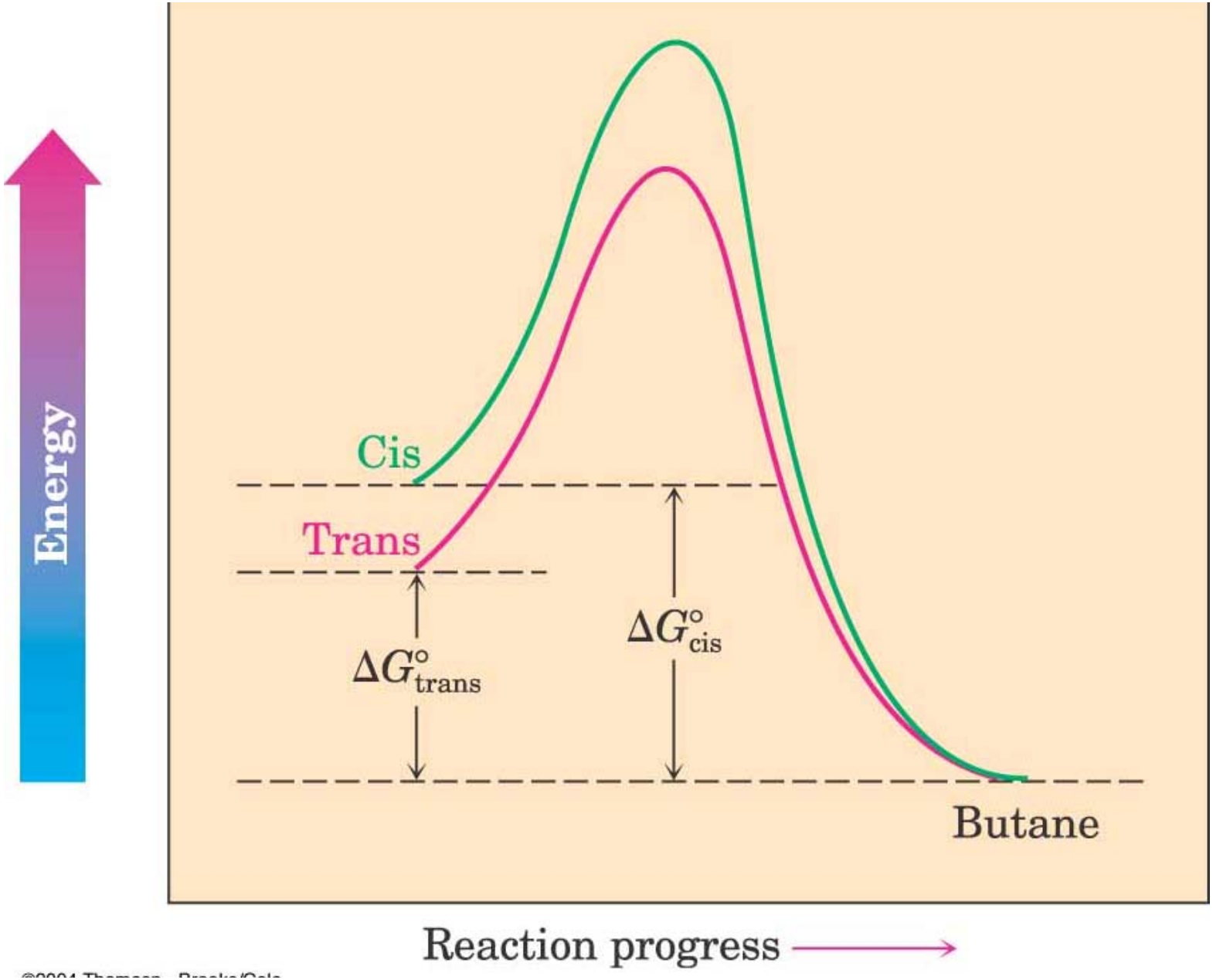
***cis*-2-Butene**

$\Delta H^\circ_{\text{combustion}} = -2685.5$ kJ/mol



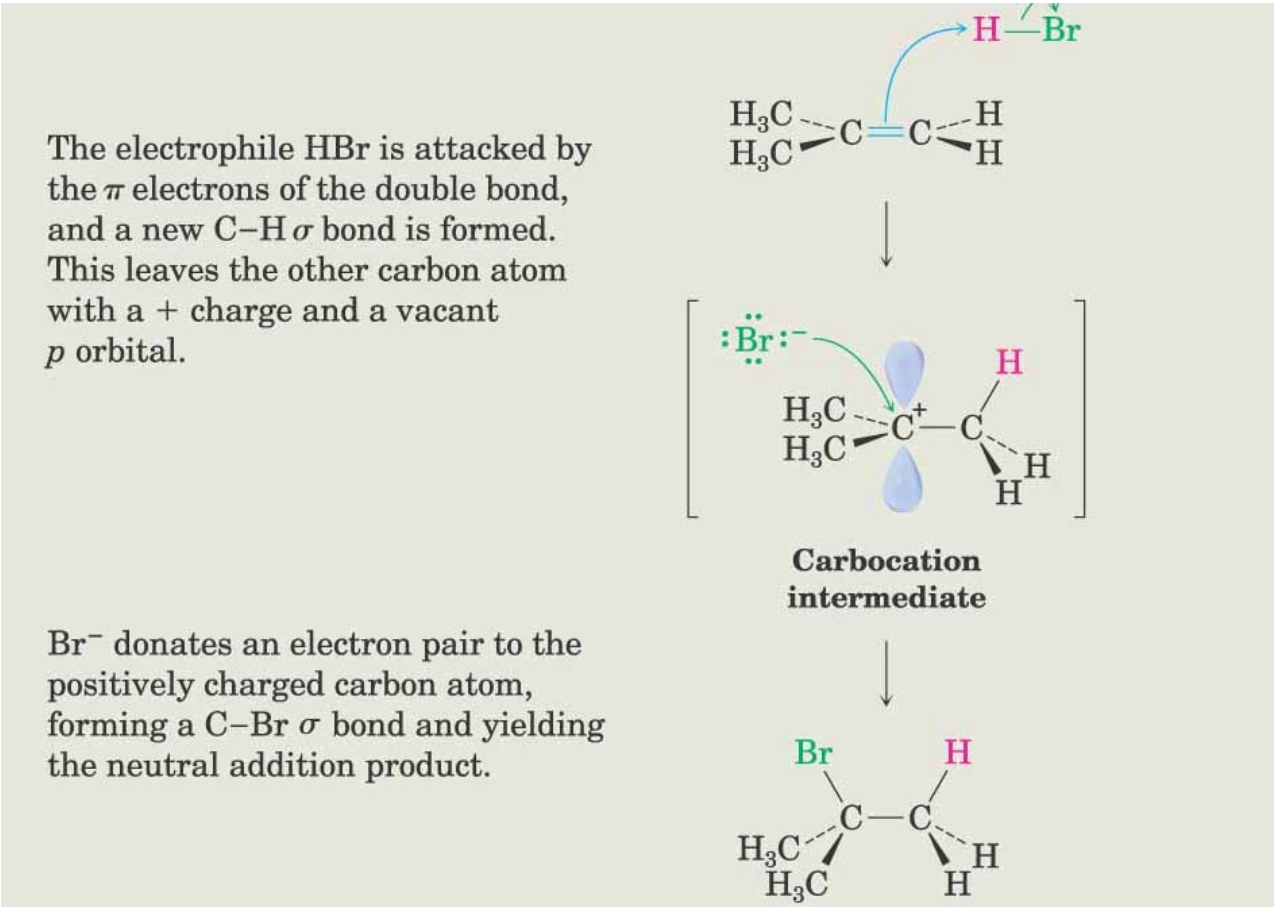
***trans*-2-Butene**

$\Delta H^\circ_{\text{combustion}} = -2682.2$ kJ/mol


Energy
Cis
Trans
ΔG°_{trans}
ΔG°_{cis}
Butane
Reaction progress

6.8 Electrophilic Addition of HX to Alkenes

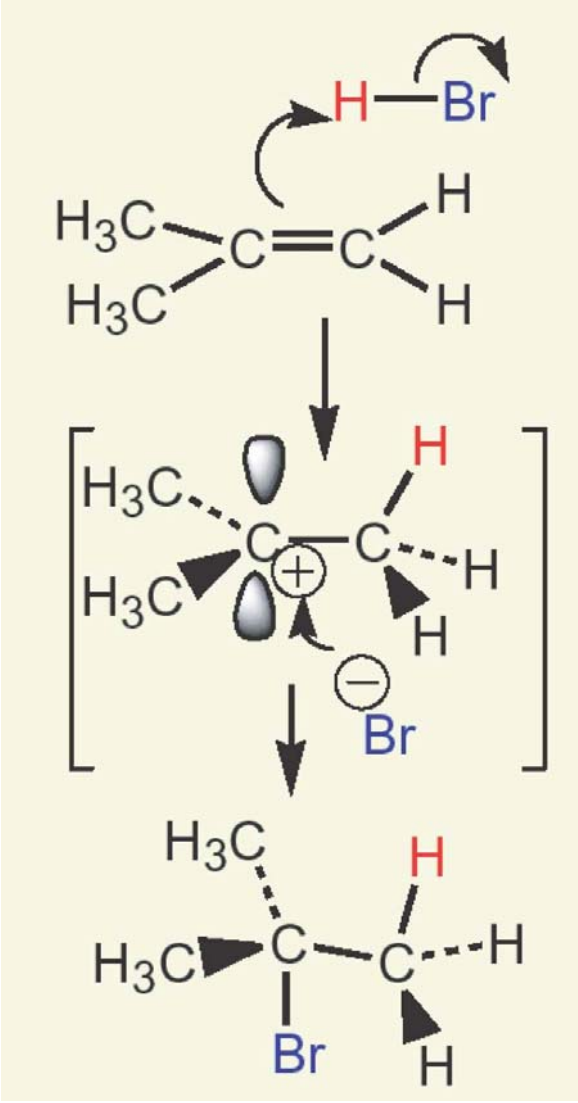
- General reaction mechanism: **electrophilic addition**
- Attack of electrophile (such as HBr) on π bond of alkene
- Produces carbocation and bromide ion
- Carbocation is an electrophile, reacting with nucleophilic bromide ion



Example of Electrophilic Addition

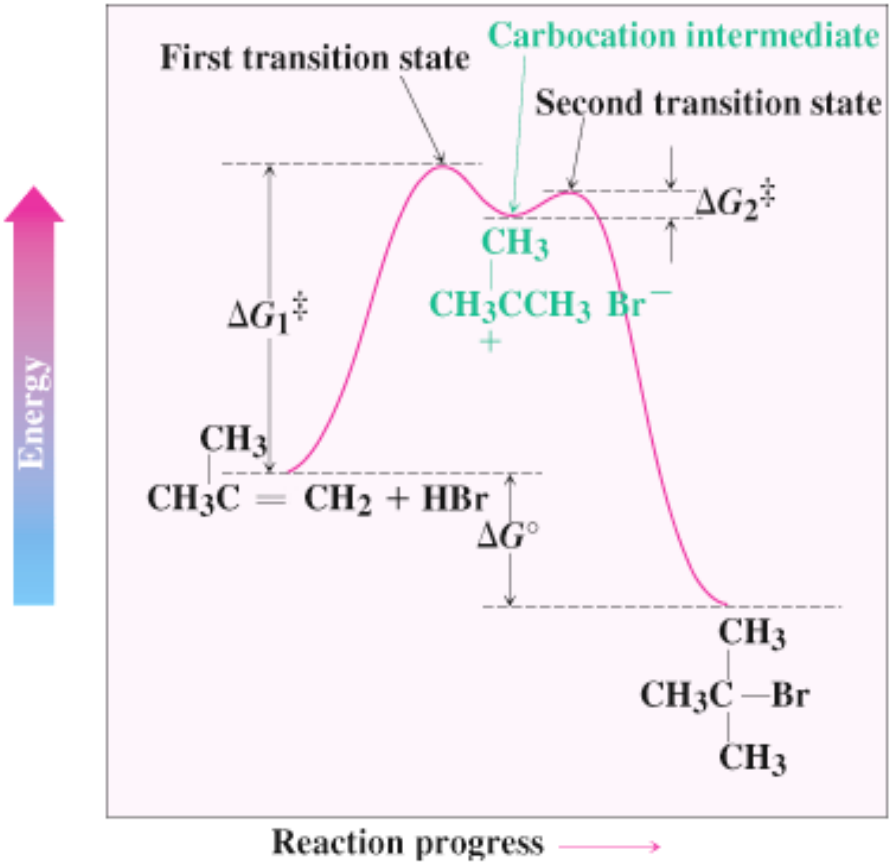
- Addition of hydrogen bromide to 2-Methyl-propene
- H-Br transfers proton to C=C
- Forms carbocation intermediate
  - More stable cation forms
- Bromide adds to carbocation

Why did the proton add to a particular carbon (the C that has 2 H's and not to the C that has 2 CH3's?)
Notice this is an unsymmetrical alkene.



Energy Diagram for Electrophilic Addition

- Rate determining (slowest, bottle neck) step has highest energy transition state
  - Independent of direction
  - In this case it is the first step in forward direction



6.9 Orientation of Electrophilic Addition: Markovnikov's Rule (addition of unsymmetrical reagent to unsymmetrical alkene)

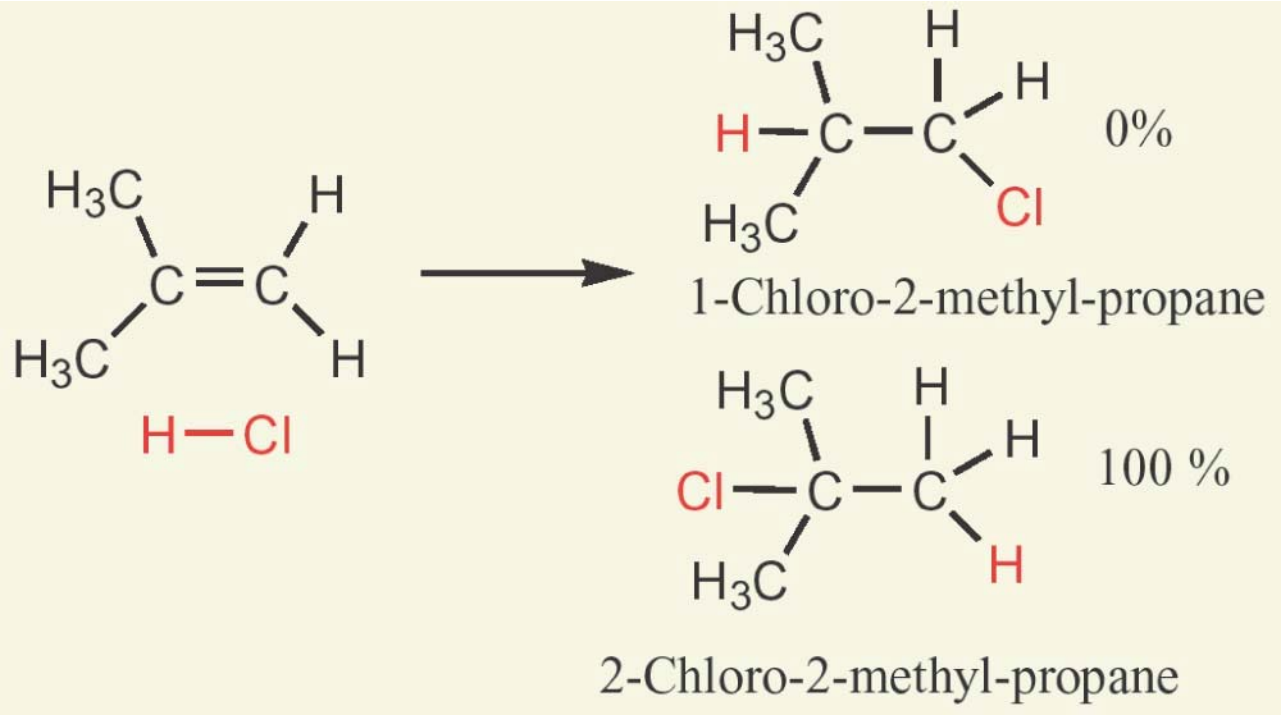
- In an unsymmetrical alkene, HX reagents can add in two different ways, but one way may be preferred over the other

- If one orientation predominates, the reaction is said to be **Regiospecific**

- Markovnikov observed in the 19th century that in the addition of HX to alkene, the H attaches to the carbon with the most H's and X attaches to the other end (to the one with the most alkyl substituents)
  - This is **Markovnikov's rule**

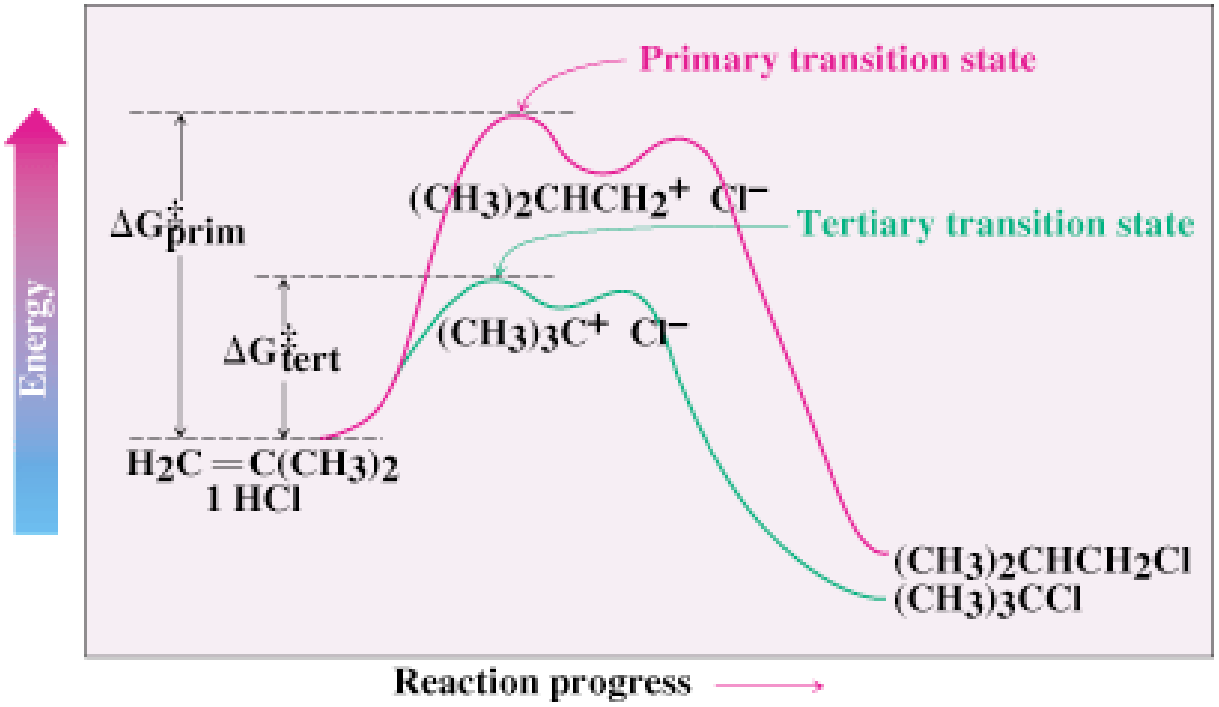
Example on Markovnikov's Rule

- Addition of HCl to 2-methylpropene
- Regiospecific – one product forms (predominantly or exclusively) where two are possible



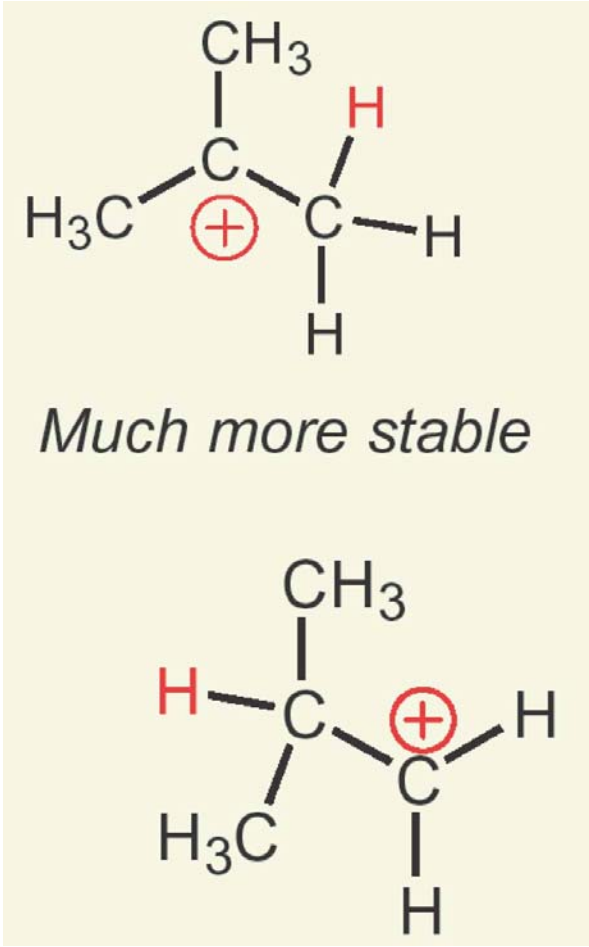
Energy of Carbocations & Markovnikov's Rule

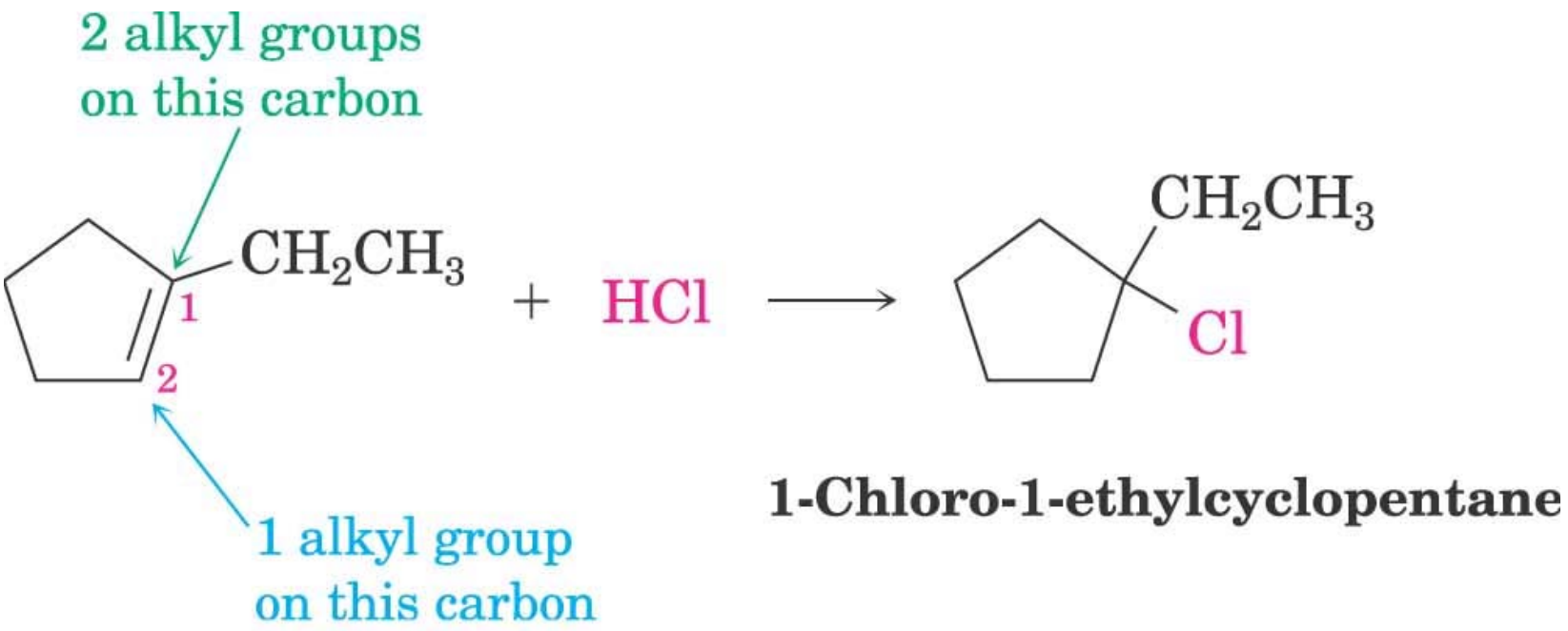
- More stable carbocation forms faster
- Tertiary carbocations and associated transition states are more stable than primary carbocations



Mechanistic Source of Regiospecificity in Addition Reactions

- If addition involves a carbocation intermediate
  - and there are two possible ways to add
  - the route producing the more alkyl substituted cationic center is lower in energy
  - alkyl groups stabilize carbocation (by virtue of being electron donating)

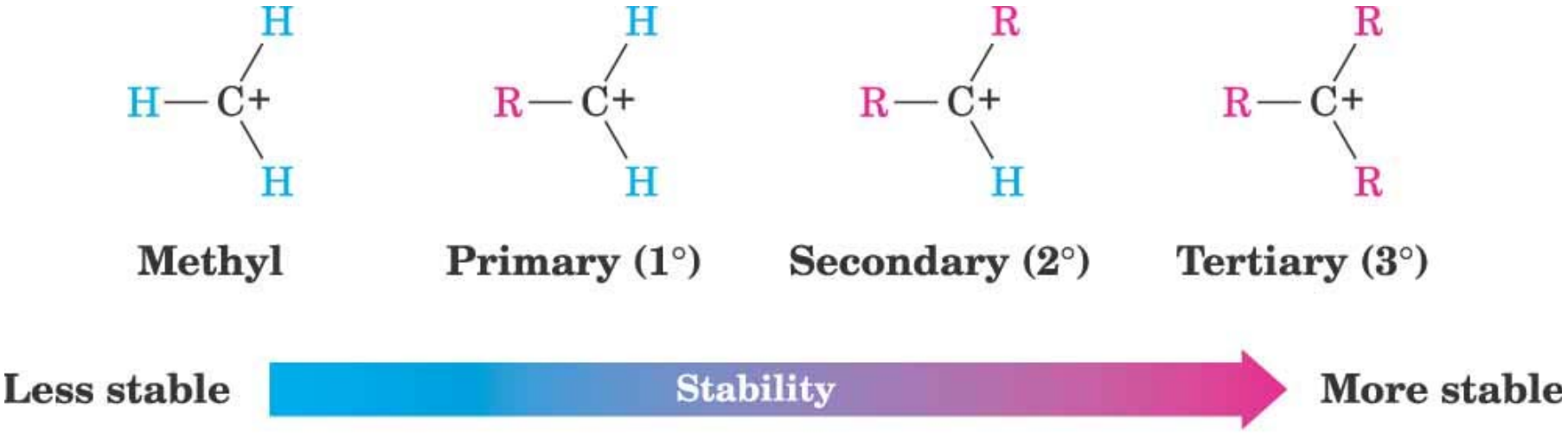


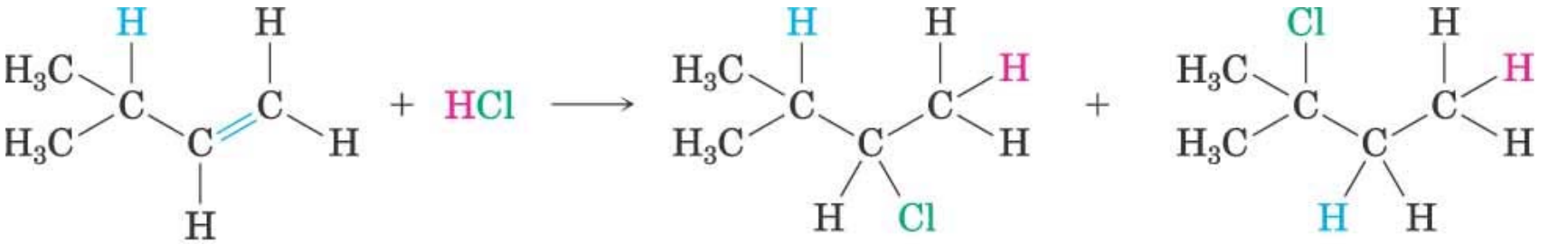


1-Chloro-1-ethylcyclopentane

6.10 Carbocation Structure and Stability

- Carbocations are planar and the tricoordinate carbon is surrounded by only 6 electrons in sp^2 orbitals
- The fourth orbital on carbon is a vacant *p*-orbital
- The stability of the carbocation (measured by energy needed to form it from R-X) is increased by the presence of alkyl substituents (electron donors)
- Therefore stability of carbocations: $3^o > 2^o > 1^o > {}^+CH_3$

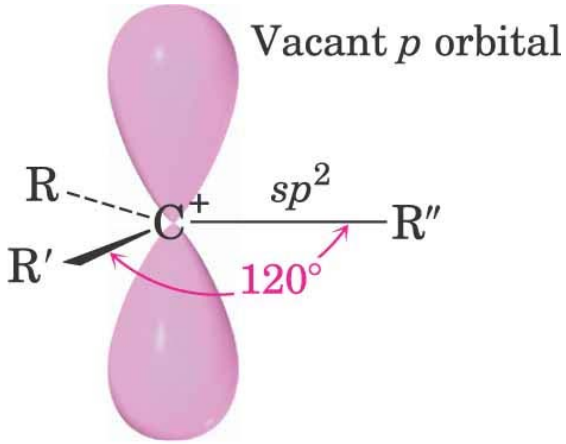


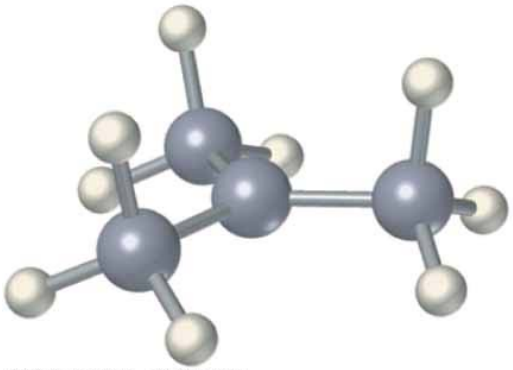


3-Methyl-1-butene

2-Chloro-3-methylbutane (approx. 50%)

2-Chloro-2-methylbutane (approx. 50%)





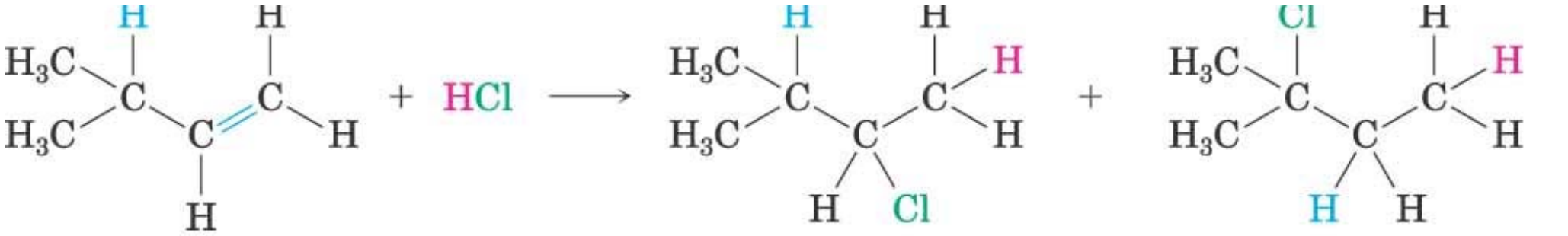
6.12 Mechanism of Electrophilic Addition: Rearrangements of Carbocations

- Carbocations undergo structural rearrangements following set patterns

- 1,2-H and 1,2-alkyl shifts occur

- Rearrangment to give more stable Carbocation

- Can go through less stable ions as intermediates



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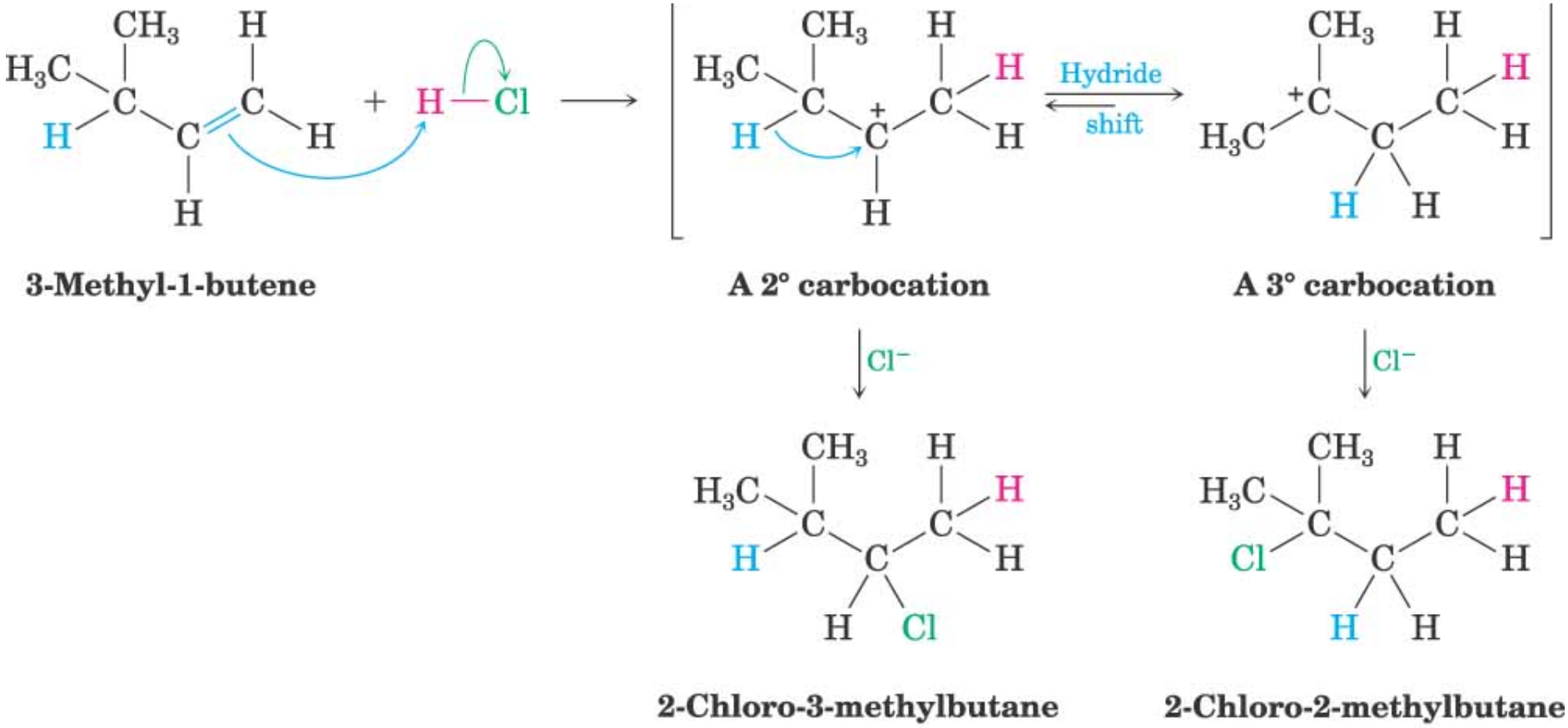
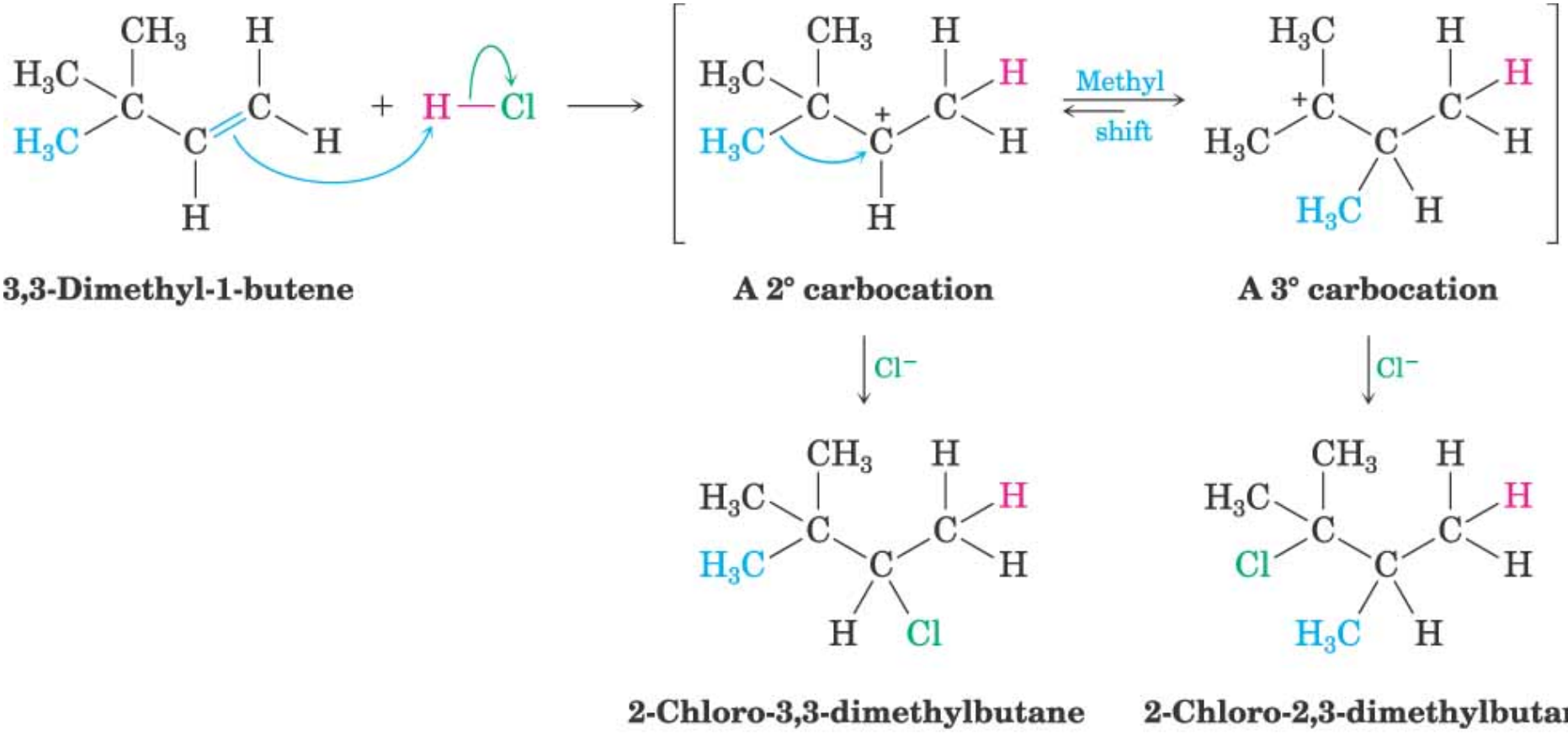
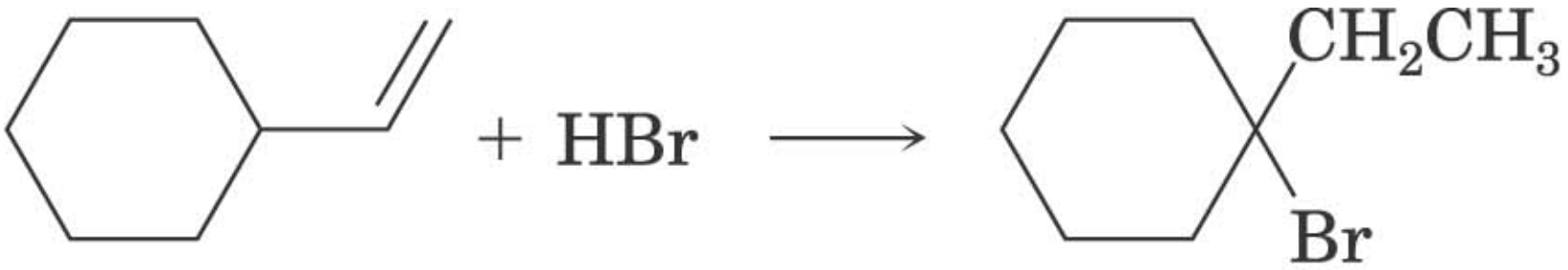




Mechanism ?



'inylcyclohexane **1-Bromo-1-ethylcyclohexan**