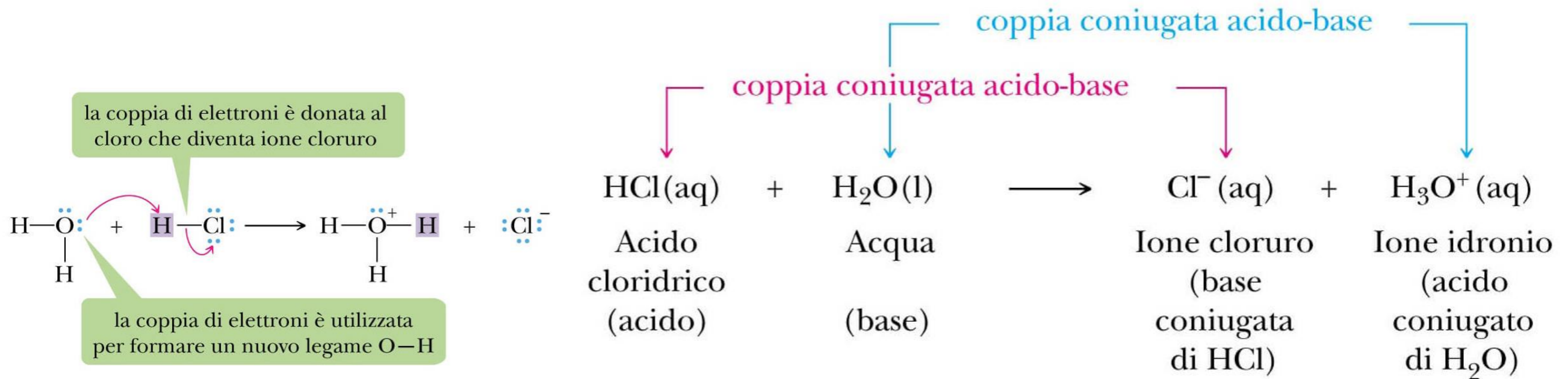


Acids and Bases
Electrophiles and Nucleophiles
Organic Reaction Mechanisms

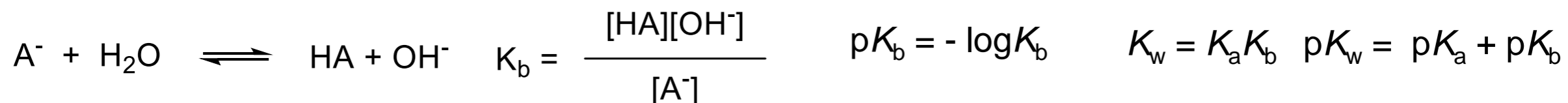
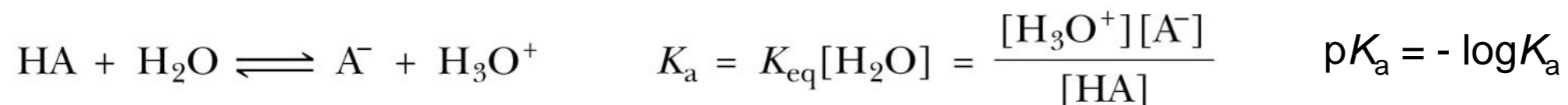
Chapters 2 & 6
Organic Chemistry, *8th Edition*
John McMurry

Acidi e basi di Brønsted-Lowry

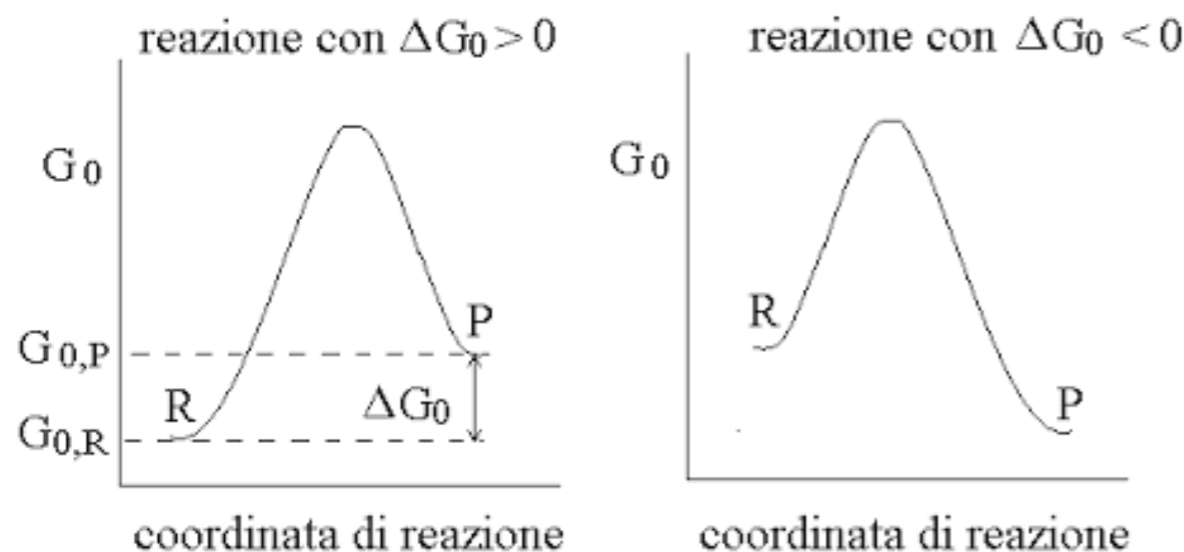
- Gli acidi donano protoni ad un accettore. Tutti gli acidi di Brønsted-Lowry contengono un protone ionizzabile.
- Le basi accettano protoni da un donatore. Tutte le basi di Brønsted-Lowry contengono un doppietto solitario o un legame π .



Acidi e basi di Brønsted-Lowry



- Più grande è la K_a (bassa $\text{p}K_a$) più l'acido è forte.
- La basicità di basi diverse si può confrontare guardando i valori di $\text{p}K_a$ dei rispettivi acidi coniugati (in chimica organica di solito si usano i valori di $\text{p}K_a$)

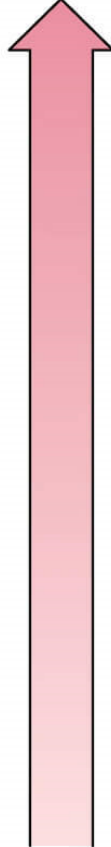
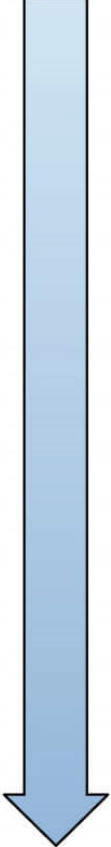


$$\Delta G^\circ = -RT \ln K$$

Equazione di van 't Hoff

Acidi e basi di Brønsted-Lowry

TABELLA 2.1 Alcuni acidi e le loro basi coniugate

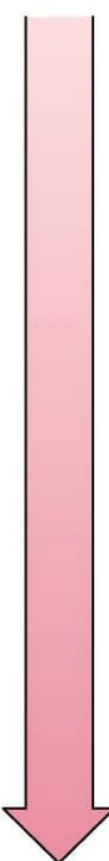
	Acido	Nome	Base coniugata	Nome	
 <p>Acidi forti</p> <p>Acidi deboli</p>	HI	Acido iodidrico	I ⁻	lone ioduro	 <p>Basi deboli</p> <p>Basi forti</p>
	HCl	Acido cloridrico	Cl ⁻	lone cloruro	
	H ₂ SO ₄	Acido solforico	HSO ₄ ⁻	lone bisolfato (idrogenosolfato)	
	HNO ₃	Acido nitrico	NO ₃ ⁻	lone nitrato	
	H ₃ O ⁺	lone idronio	H ₂ O	Acqua	
	HSO ₄ ⁻	lone bisolfato	SO ₄ ²⁻	lone solfato	
	H ₃ PO ₄	Acido fosforico	H ₂ PO ₄ ⁻	lone fosfato biacido	
	CH ₃ COOH	Acido acetico	CH ₃ COO ⁻	lone acetato	
	H ₂ CO ₃	Acido carbonico	HCO ₃ ⁻	lone bicarbonato	
	H ₂ S	Acido solfidrico	HS ⁻	lone bisolfuro	
	H ₂ PO ₄ ⁻	lone fosfato biacido	HPO ₄ ²⁻	lone fosfato monoacido	
	NH ₄ ⁺	lone ammonio	NH ₃	Ammoniaca	
	HCN	Acido cianidrico	CN ⁻	lone cianuro	
	C ₆ H ₅ OH	Fenolo	C ₆ H ₅ O ⁻	lone fenossido	
	HCO ₃ ⁻	lone bicarbonato	CO ₃ ²⁻	lone carbonato	
	HPO ₄ ²⁻	lone fosfato monoacido	PO ₄ ³⁻	lone fosfato	
	H ₂ O	Acqua	OH ⁻	lone idrossido	
C ₂ H ₅ OH	Etanolo	C ₂ H ₅ O ⁻	lone etossido		

Acidi e basi di Brønsted-Lowry

TABELLA 2.2 Valori di pK_a di alcuni acidi organici e inorganici

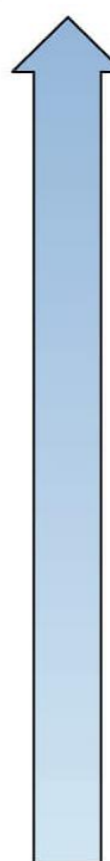
	Acido	Formula	pK_a	Base coniugata	
	Etano	CH_3CH_3	51	$CH_3CH_2^-$	
	Ammoniaca	NH_3	38	NH_2^-	
	Etanolo	CH_3CH_2OH	15.9	$CH_3CH_2O^-$	
	Acqua	H_2O	15.7	HO^-	
	Ione metilammonio	$CH_3NH_3^+$	10.64	CH_3NH_2	
	Ione bicarbonato	HCO_3^-	10.33	CO_3^{2-}	
	Fenolo	C_6H_5OH	9.95	$C_6H_5O^-$	
	Ione ammonio	NH_4^+	9.24	NH_3	
	Acido cianidrico	HCN	9.21	CN^-	
	Acido carbonico	H_2CO_3	6.36	HCO_3^-	
	Acido acetico	CH_3COOH	4.76	CH_3COO^-	
	Acido benzoico	C_6H_5COOH	4.19	$C_6H_5COO^-$	
	Acido fosforico	H_3PO_4	2.1	$H_2PO_4^-$	
	Ione idronio	H_3O^+	-1.74	H_2O	
	Acido solforico	H_2SO_4	-5.2	HSO_4^-	
	Acido cloridrico	HCl	-7	Cl^-	
	Acido bromidrico	HBr	-8	Br^-	
	Acido iodidrico	HI	-9	I^-	

Acido più debole



Acido più forte

Base più forte




Base più debole

Acidi e basi di Brønsted-Lowry

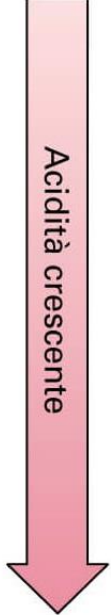


quando si confrontano *atomi appartenenti allo stesso periodo* della Tavola Periodica carichi negativamente, **quanto più elettronegativo è l'atomo tanto meglio esso sopporta la carica negativa**

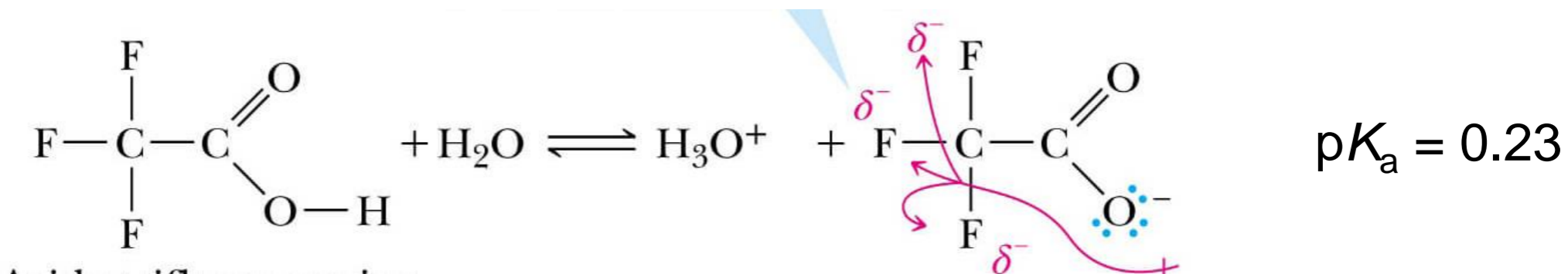
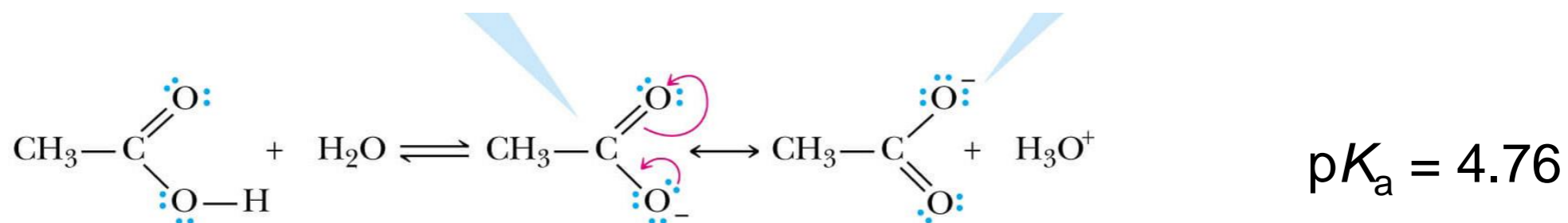
	H ₃ C—H	H ₂ N—H	HO—H	F—H
pK _a	51	38	15.7	3.5
Elettronegatività di A in A—H	2.5	3.0	3.5	4.0



Acido	Base coniugata	pKa
HF	F ⁻	3.5
HCl	Cl ⁻	-7
HBr	Br ⁻	-8
HI	I ⁻	-9
H ₂ O	OH ⁻	15.7
H ₂ S	SH ⁻	7.05



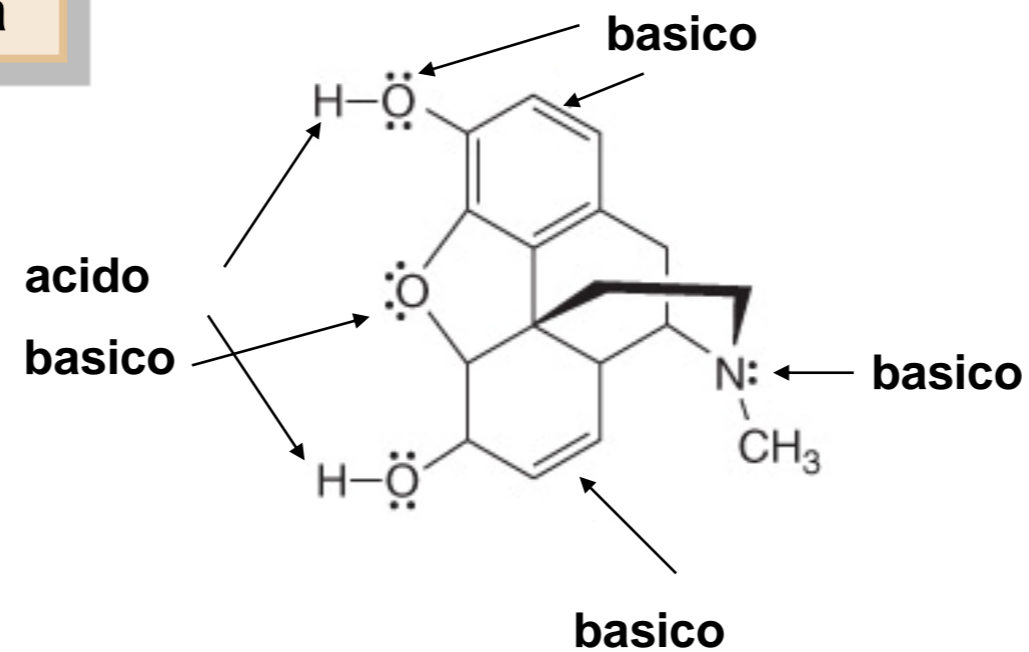
Acidi e basi di Brønsted-Lowry



Acidi e basi di Brønsted-Lowry

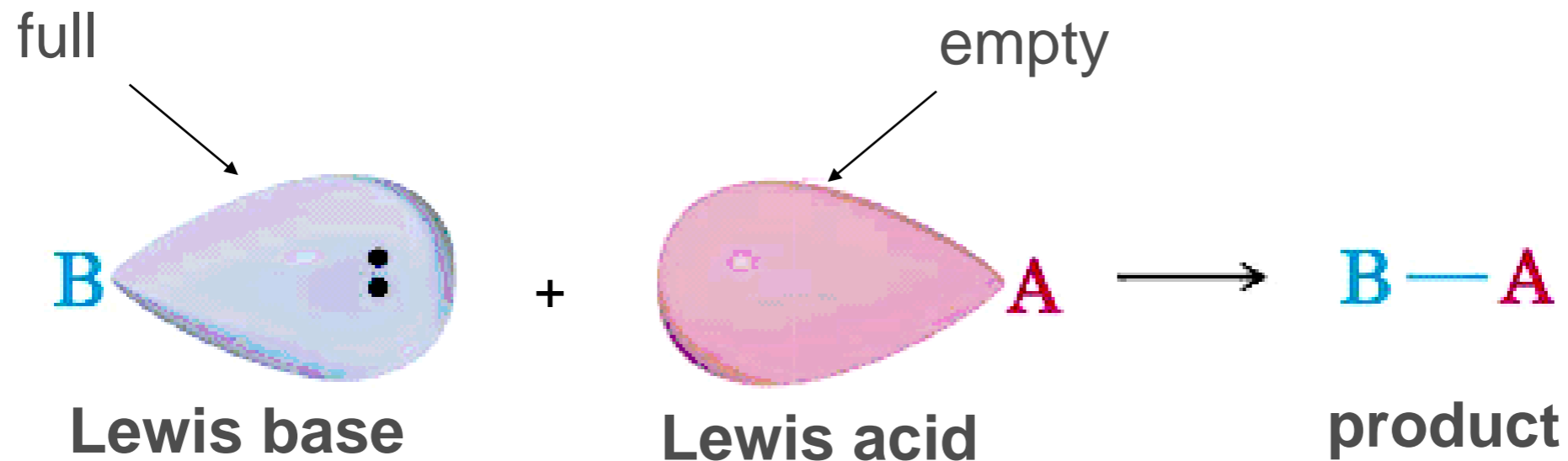
Molecole organiche complesse hanno molti siti acidi o basici

Morfina



Lewis Acids and Bases

- A Lewis acid accepts an electron pair from a donor. Lewis acids have a low energy empty orbital.
- A Lewis base donates an electron pair to an acceptor. Lewis bases have a high energy full orbital (lone pair or π bonds).



Lewis Acids and Bases

- All Brønsted-Lowry acids are Lewis acids. Not all Lewis acids are Brønsted-Lowry acids.
- Only species with ionizable protons are Brønsted-Lowry acids. Any electron acceptor is a L.A.

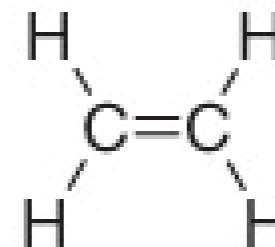
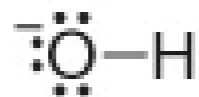


Brønsted-Lowry **and** Lewis acids



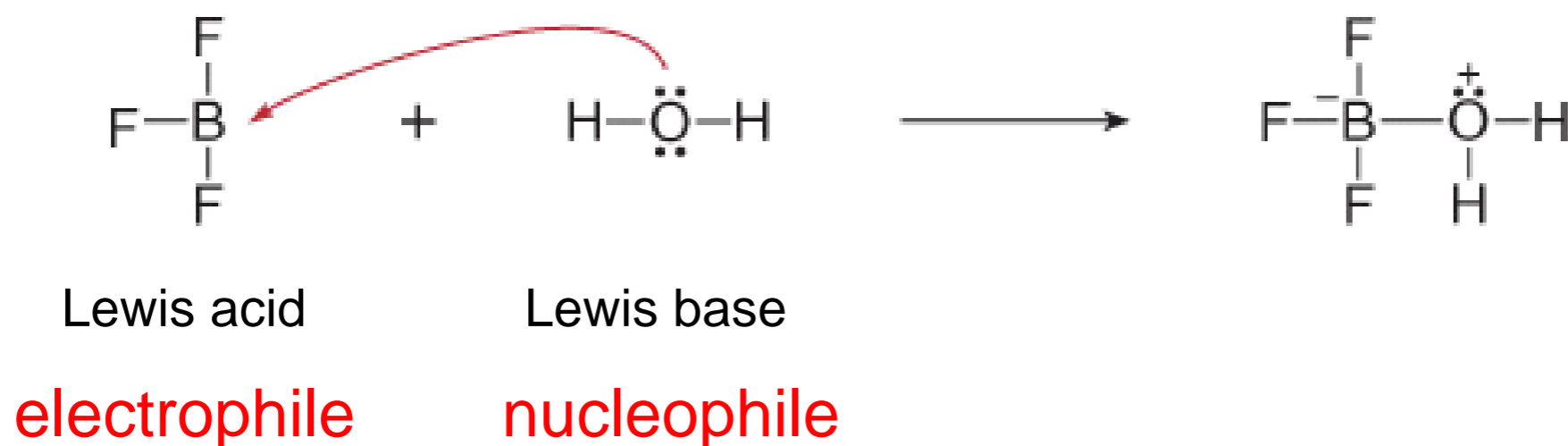
Lewis acids

- All Brønsted-Lowry bases are also Lewis bases. They must have either a lone pair or a π bond.



Reactions Between Lewis Acids and Bases

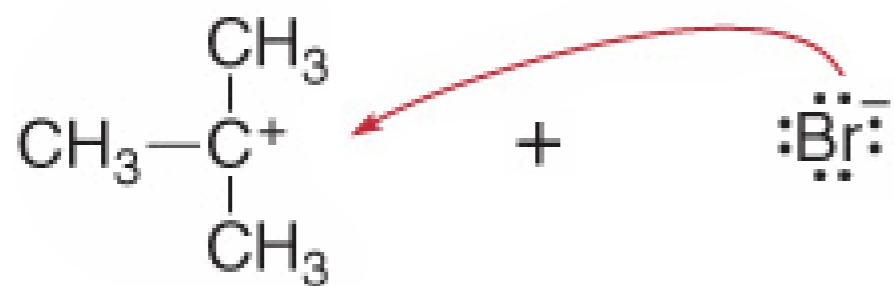
- Organic reactions can in most cases be described as reactions between electron poor species (Lewis acids) and electron rich species (Lewis bases).
- The electron poor species (Lewis acid) is called **electrophile**.
- The electron rich species (Lewis base) is called **nucleophile**.
- The movement of electrons is indicated with curved arrows.



Electrophiles and Nucleophiles

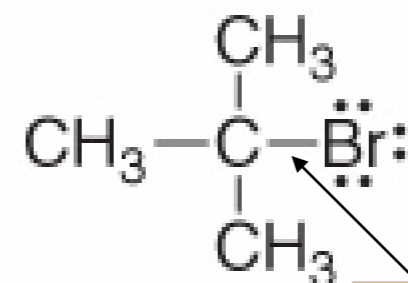
electrophile

nucleophile

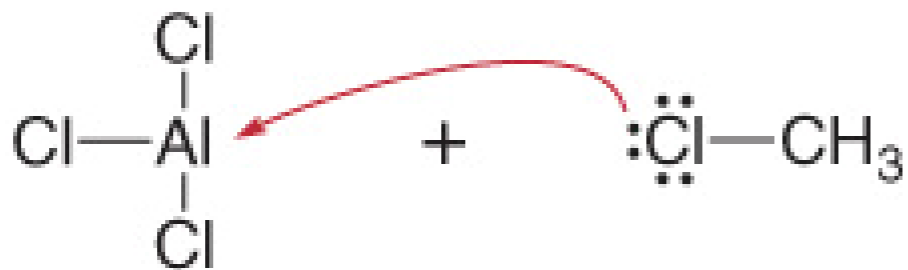


Lewis acid

Lewis base

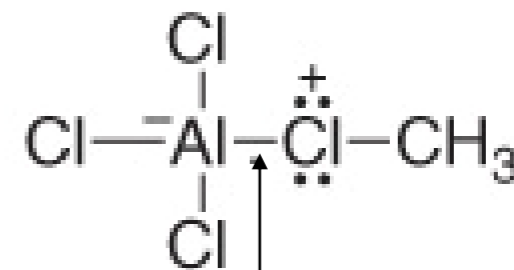


New bond



Lewis acid

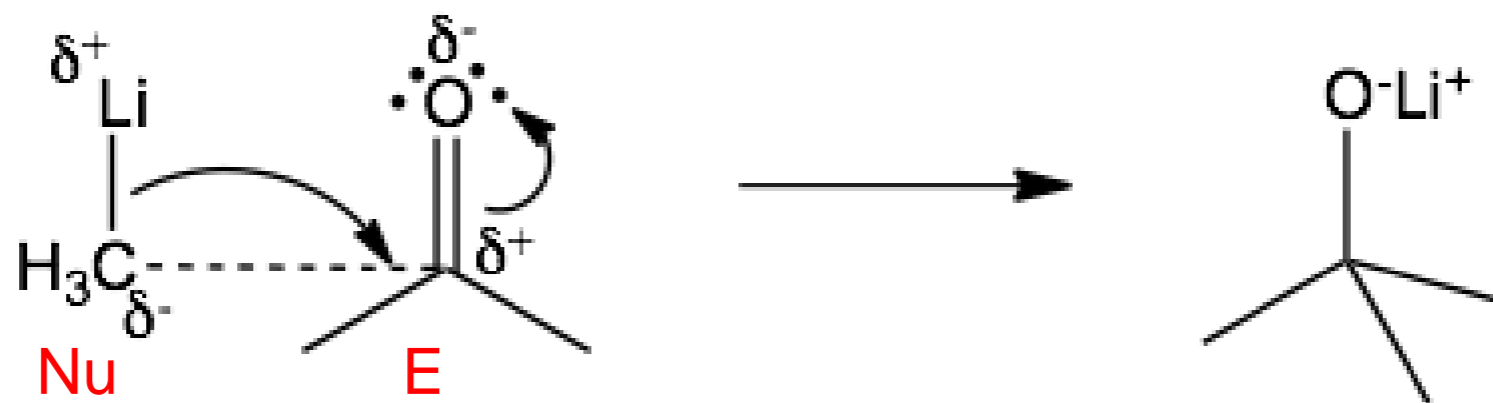
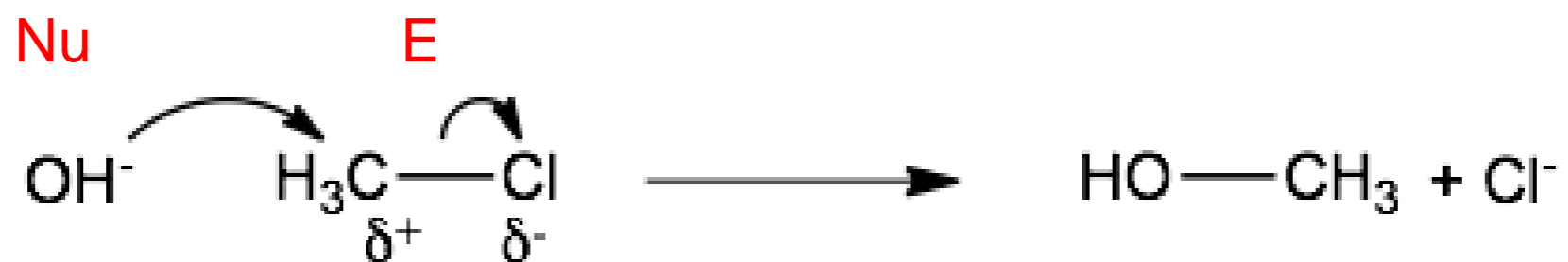
Lewis base



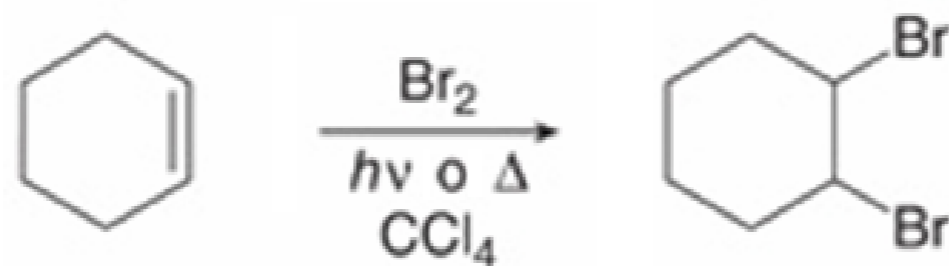
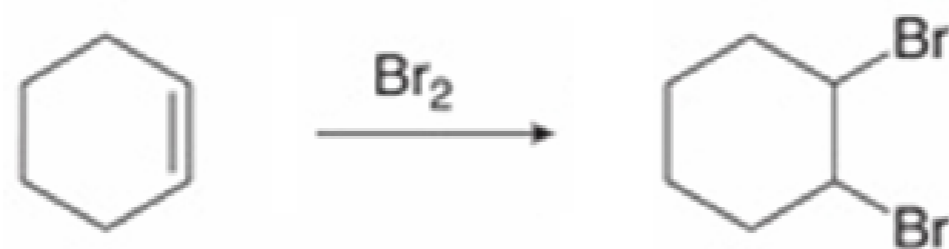
New bond

Electrophiles and Nucleophiles

- Nucleophiles and electrophiles may also contain polarized bonds

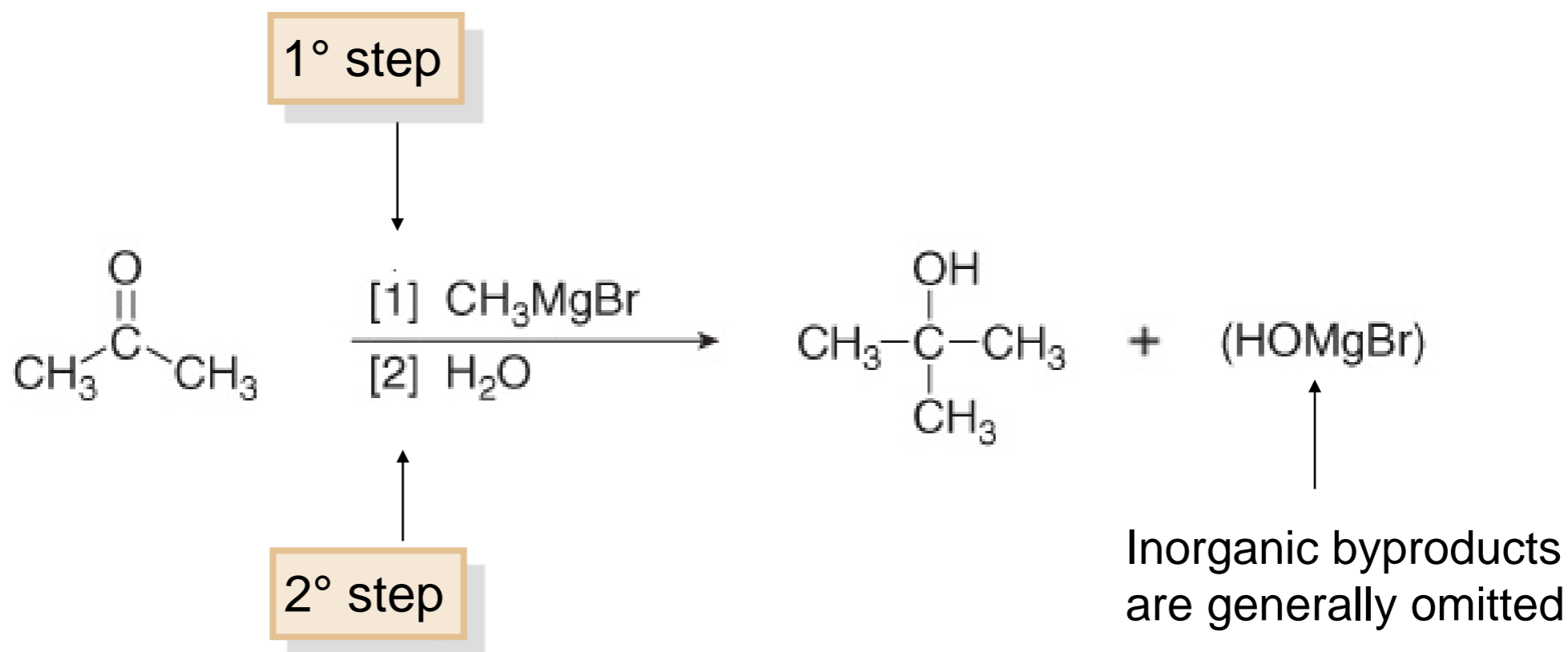


How to Write an Organic Reaction



How to Write an Organic Reaction

In a sequence, the individual steps are numbered.

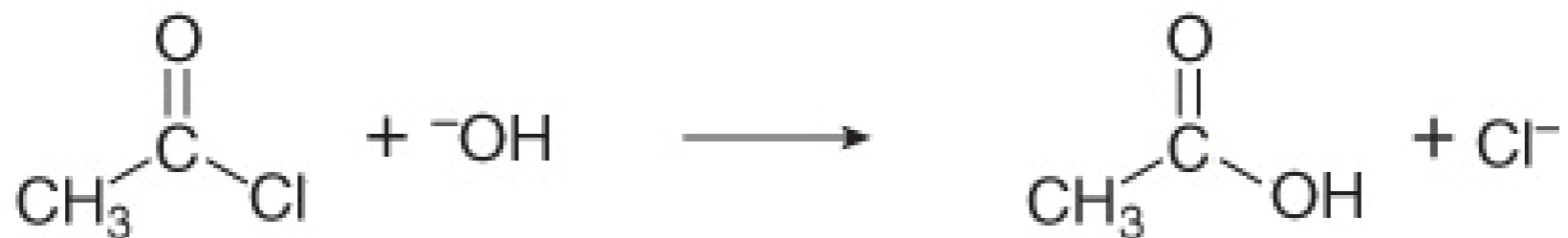
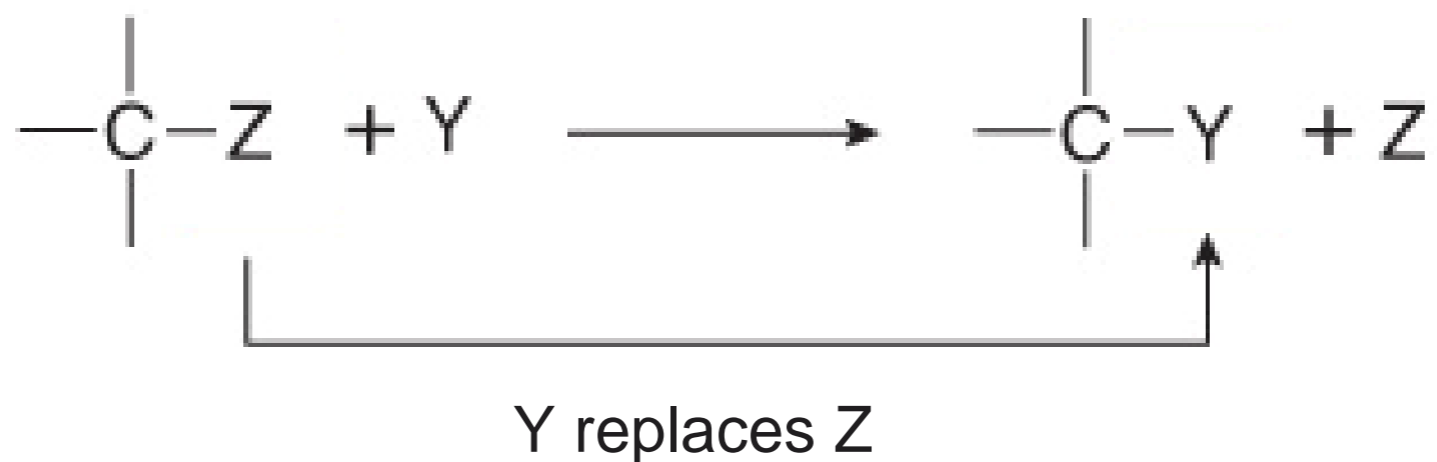


Organic Reactions

- Type of reaction (bond breaking/bond formation):
 - substitution
 - addition
 - elimination
 - rearrangement/transposition
- Mechanism = movement of electrons:
 - ionic (polar)
 - radicalic
 - pericyclic

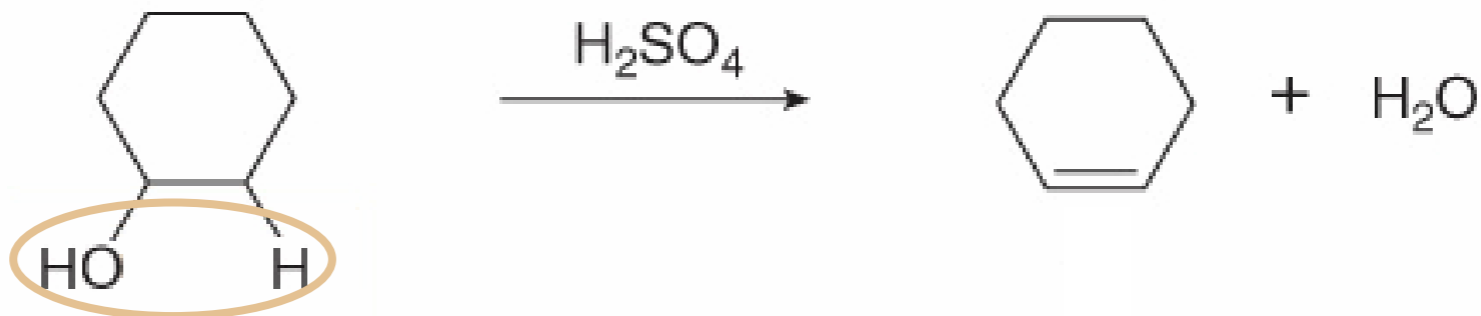
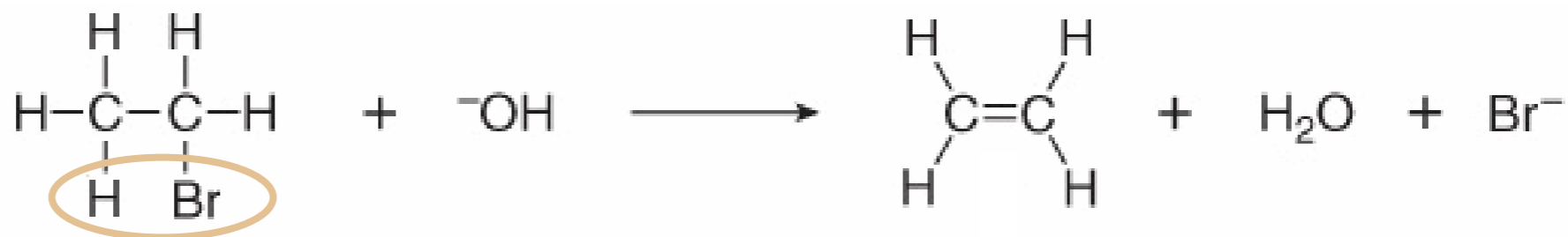
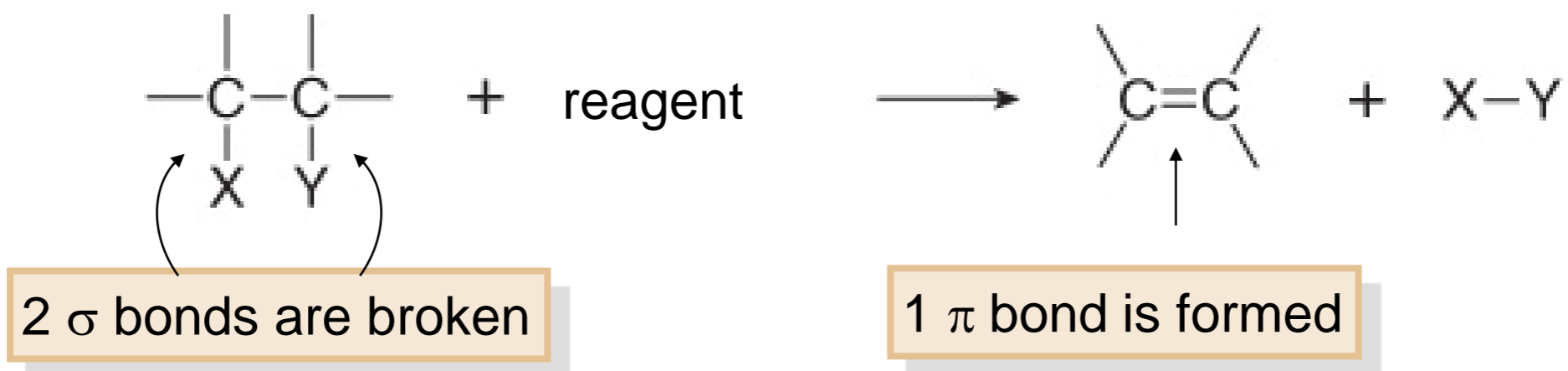
Substitutions

- In a general substitution reaction, an atom or group Y replaces an atom or group Z at carbon.
- Substitutions involve breaking and forming σ bonds.



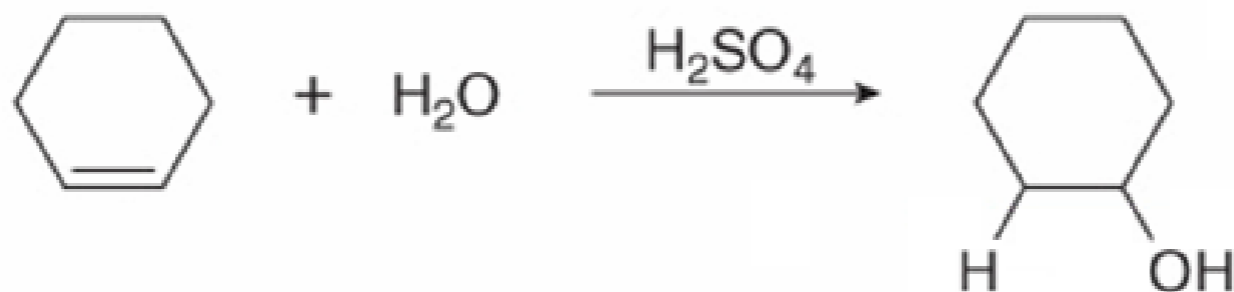
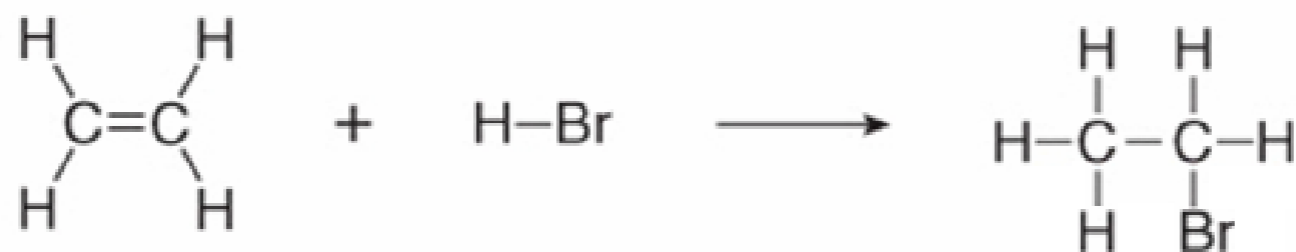
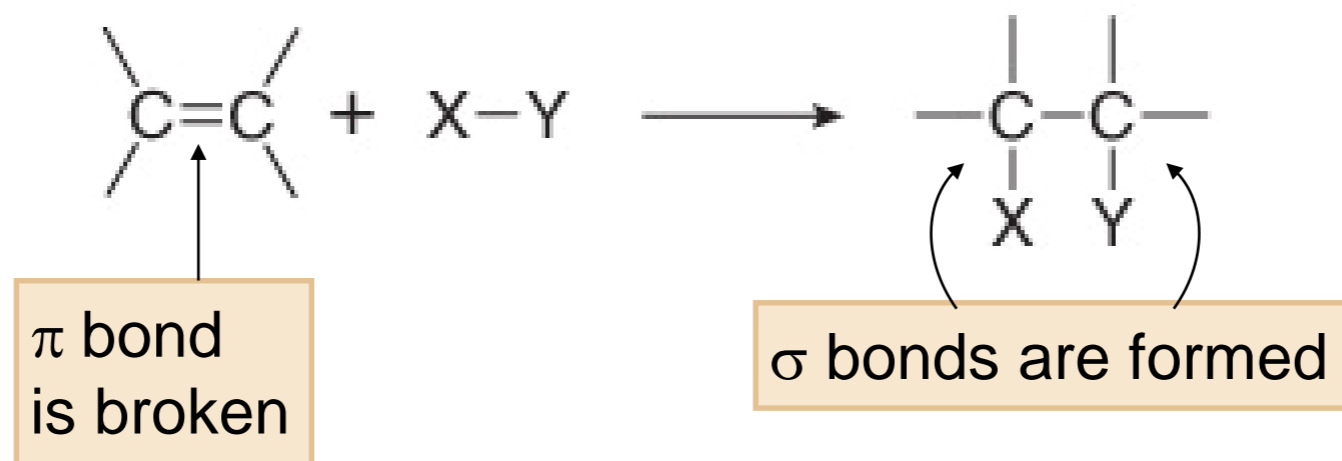
Eliminations

In an **elimination** reaction two σ bonds are broken and one π bond is formed.



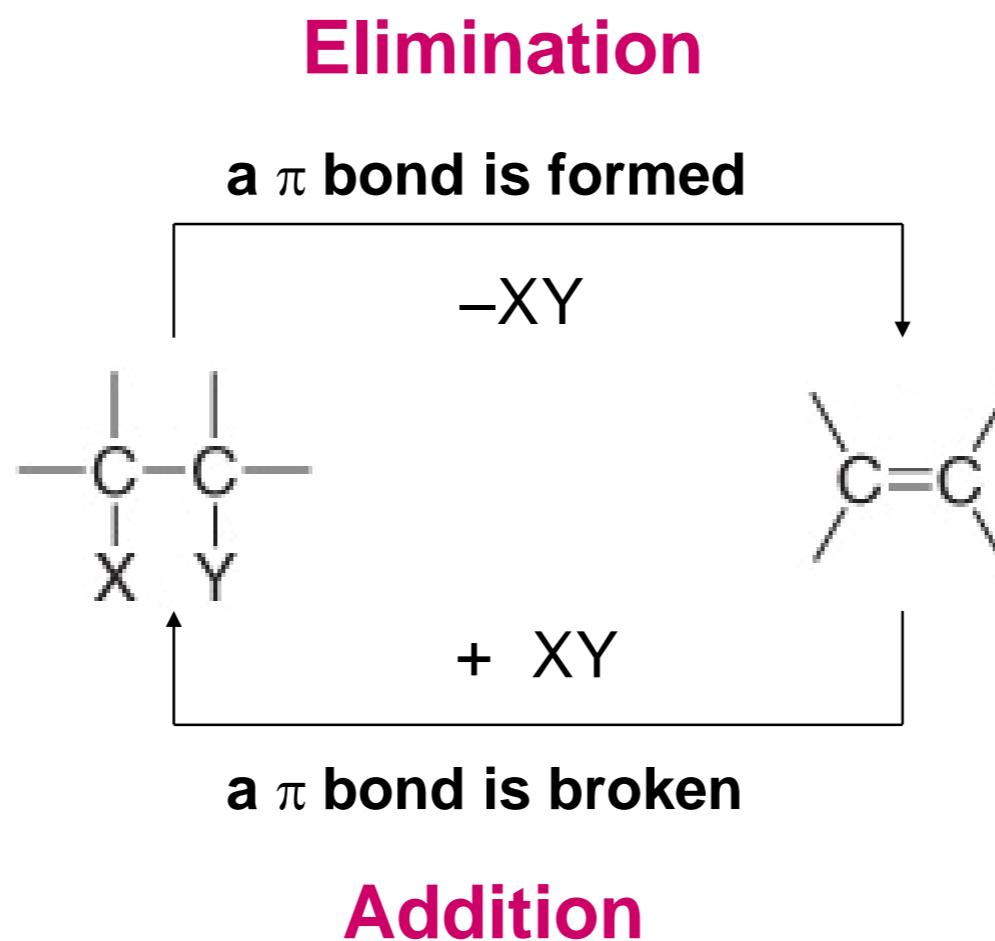
Additions

In an **addition** reaction a π bond is broken and two new σ bond are formed.



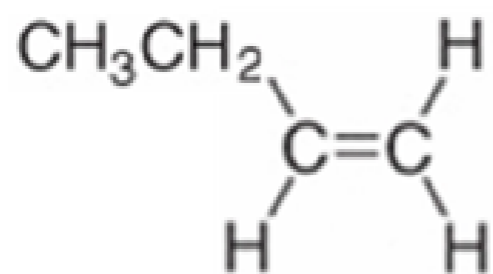
Additions and Eliminations

- Eliminations are the inverse of additions. A π bond is formed in eliminations and a π bond is broken in additions.

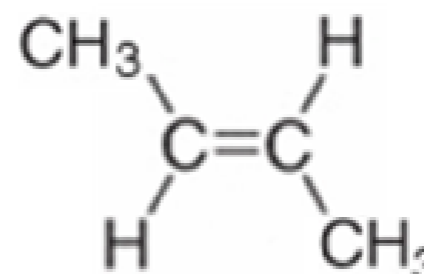


Rearrangements or Transpositions

In a rearrangement or transposition the bonding pattern of a single reagent changes giving a constitutional isomer.

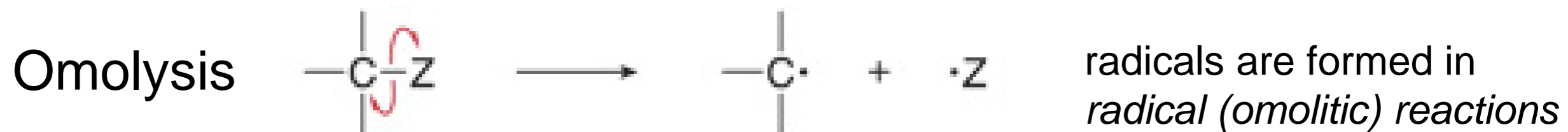


1-butene



2-butene

Bond Breaking and Forming



Radical



Carbocation

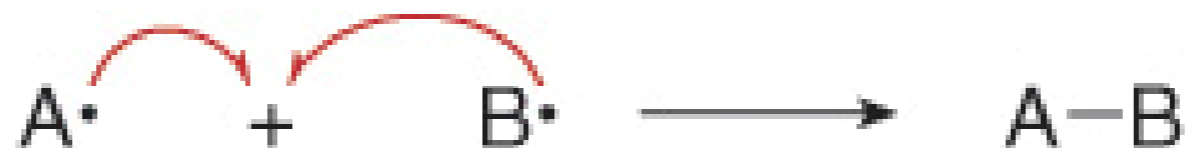
ions are formed or react in *polar (ionic) reactions*



Carbanion

Bond Formation

- A new bond can be formed in two ways:
 - From two radicals each contributing a single electron.



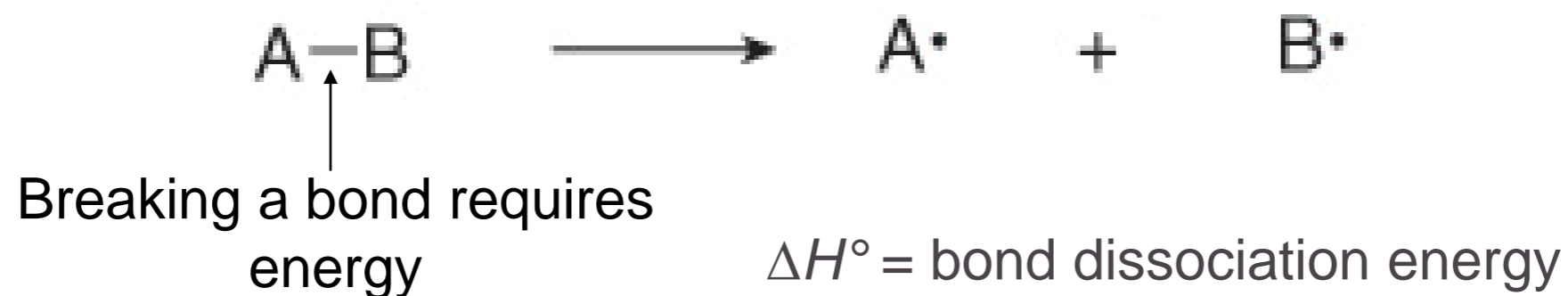
- From a nucleophile contributing an electron pair and an electrophile accepting the electron pair. Nu and E may be ions or neutral molecules



Energy is released in the formation of a bond

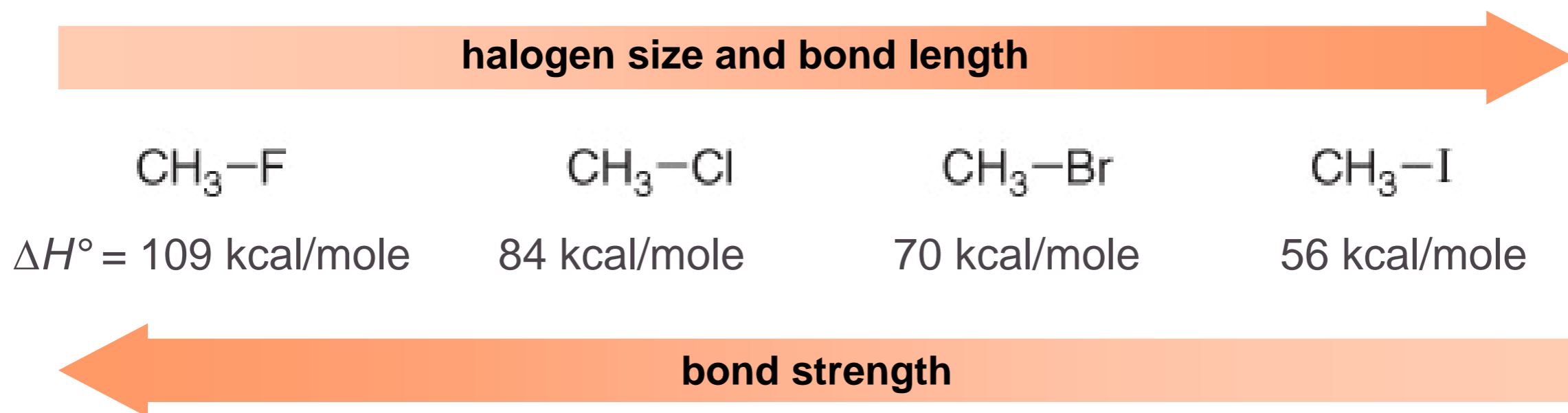
Bond Dissociation Energy

Bond dissociation energy is the energy necessary to break a bond homolytically.



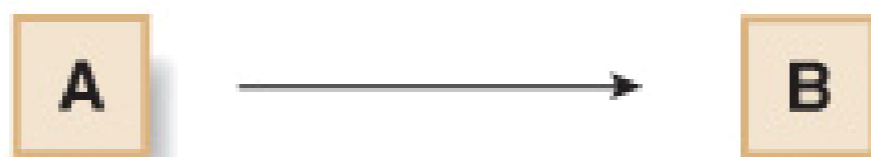
Bond Dissociation Energy

- The bond dissociation energy is a measure of the strength of the bond.
- The stronger the bond, the higher its dissociation energy.
- In general, shorter bonds are stronger.
- Bond dissociation energies decrease along a group.



A Reaction Mechanism.....

- Accounts for all reagents and products and their ratios.
- Describes in which order bonds are broken and formed and the rates of individual steps.
- In a *concerted reaction* reagents are directly converted into products in a single step.

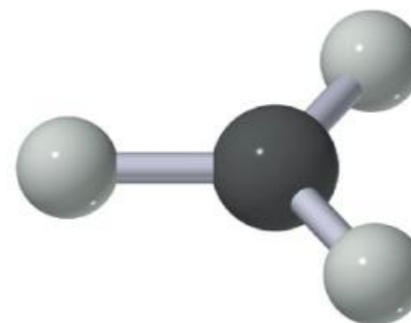
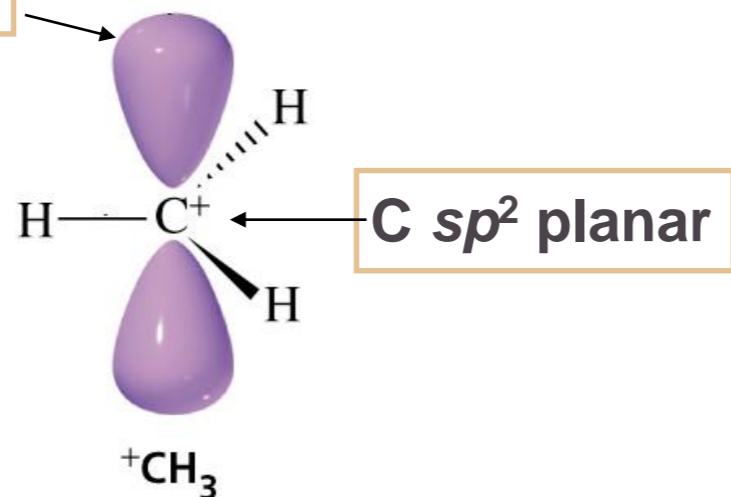


- A multistep reaction involves the formation of one or more reactive intermediates.

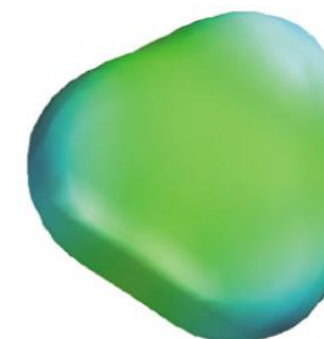
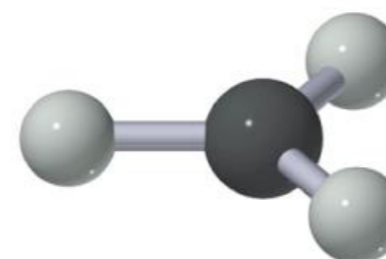
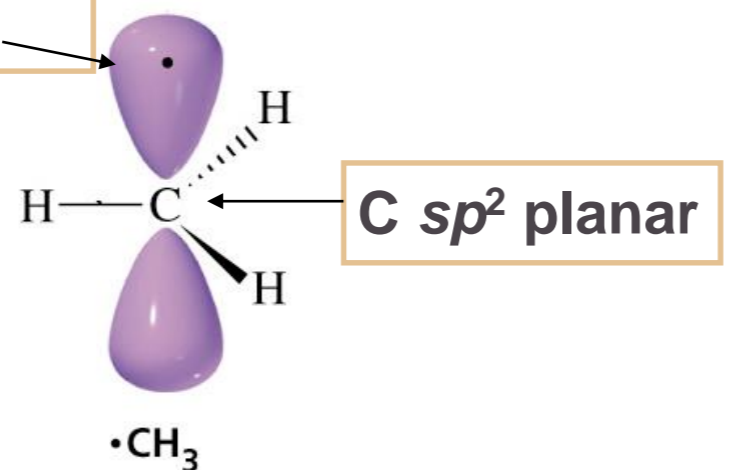


Carbocations, Carbanions, Radicals

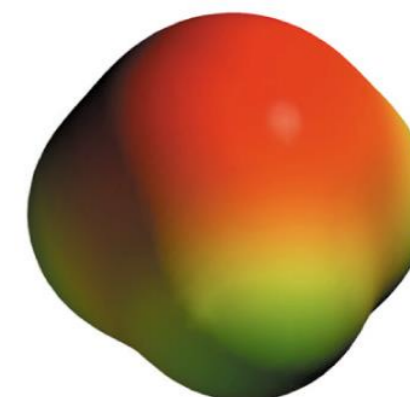
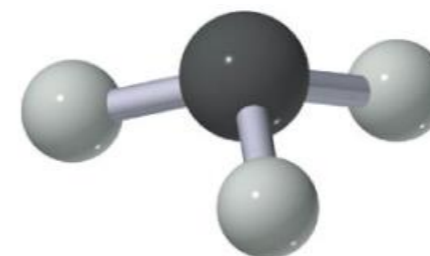
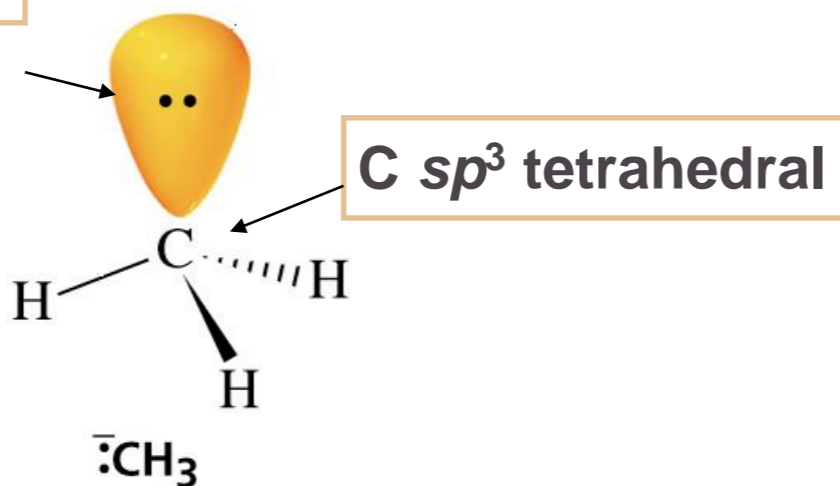
empty p orbital



Singly occupied p orbital

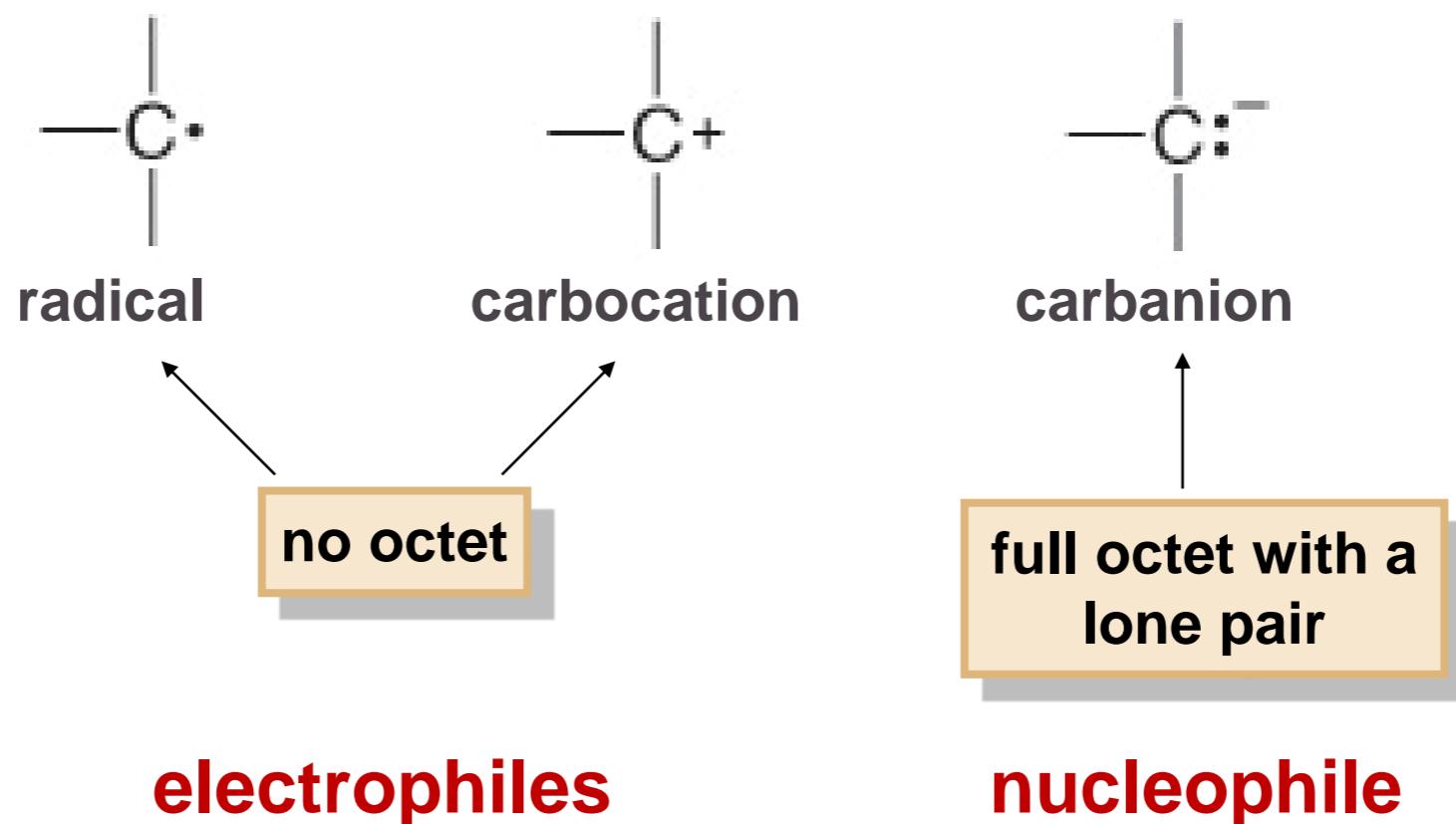


lone pair sp^3

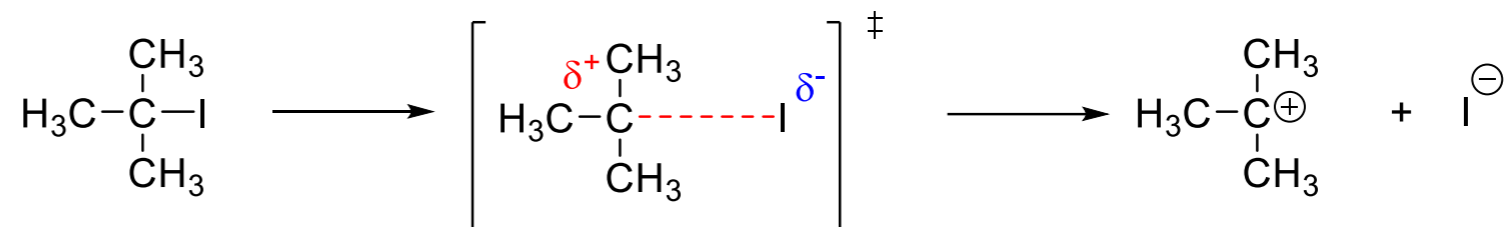
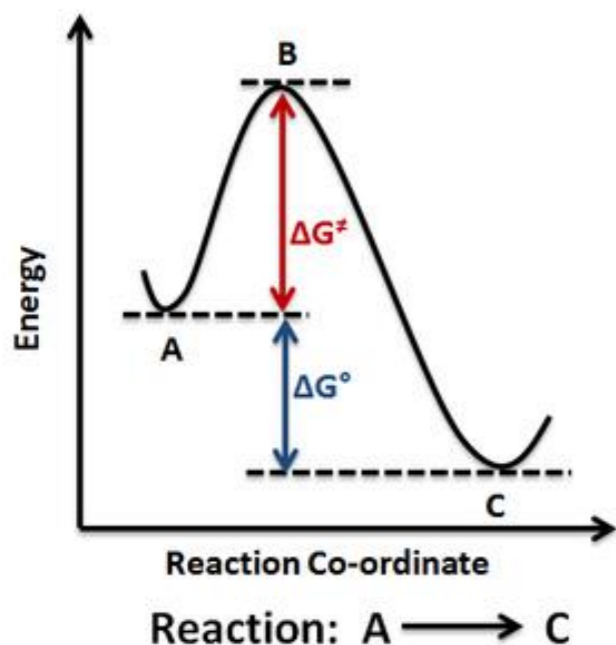


Carbocations, Carbanions, Radicals

- Radicals and carbocations are **electrophiles** because the carbon atom does not have a full octet.
- Carbanions are **nucleophiles** because the carbon atom has a lone pair.

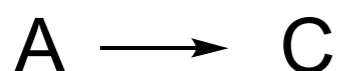


Transition State Theory - Energy Diagrams



the reaction coordinate is the length of the C-I bond

- The energy diagram describes the geometric transformation of reactants into products.
- Each point of the energy diagram represent a particular geometry of the reactant system
- The transition state structure is the one at highest energy and its structure is intermediate between the structures of reagents and products..



$$v = d[\text{C}]/dt = k [\text{A}]$$

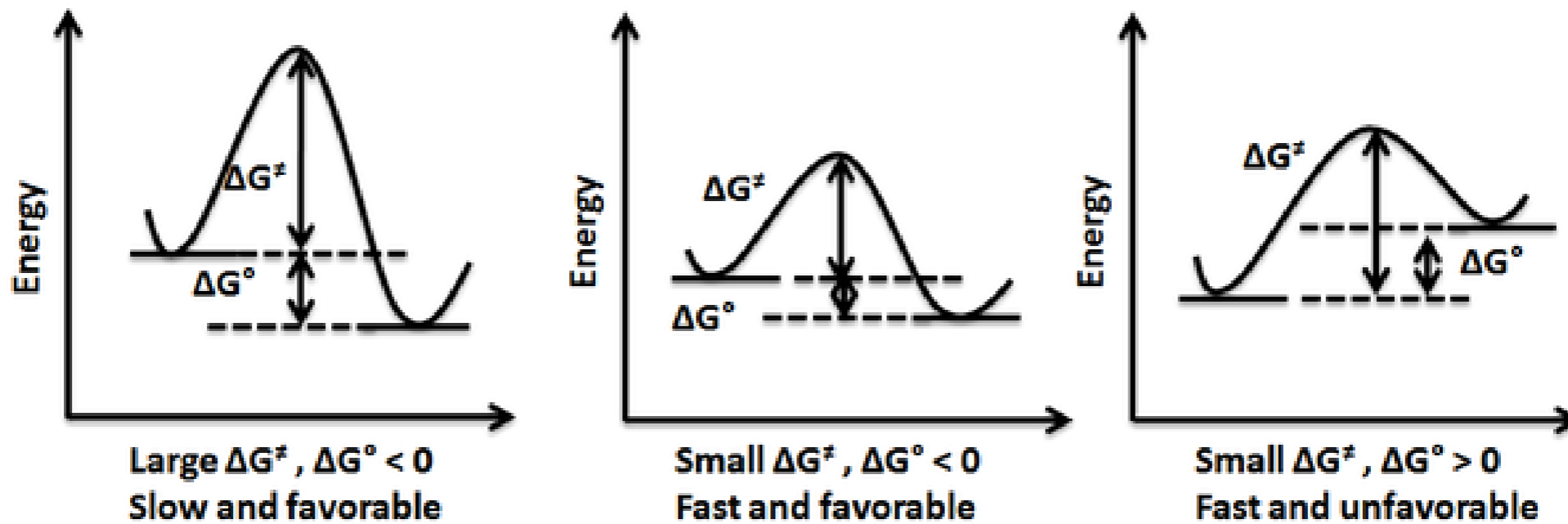
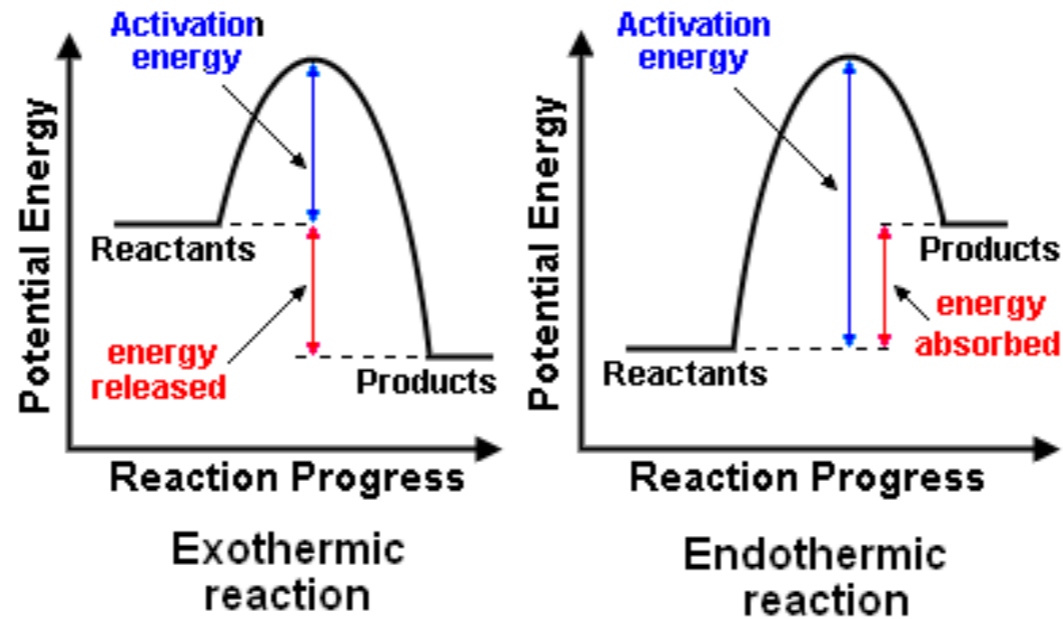
$$k = \frac{k_B T}{h} e^{-\frac{\Delta G^\ddagger}{RT}}$$

Eyring equation

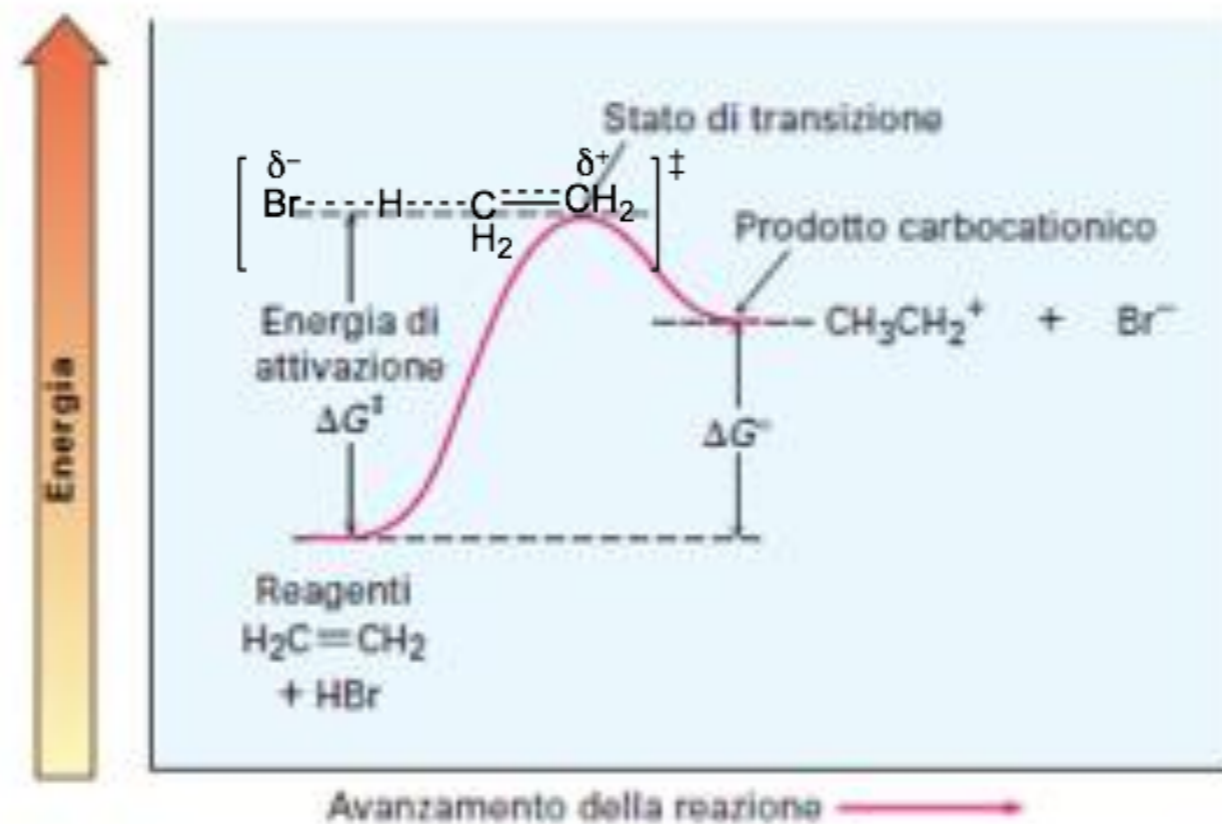
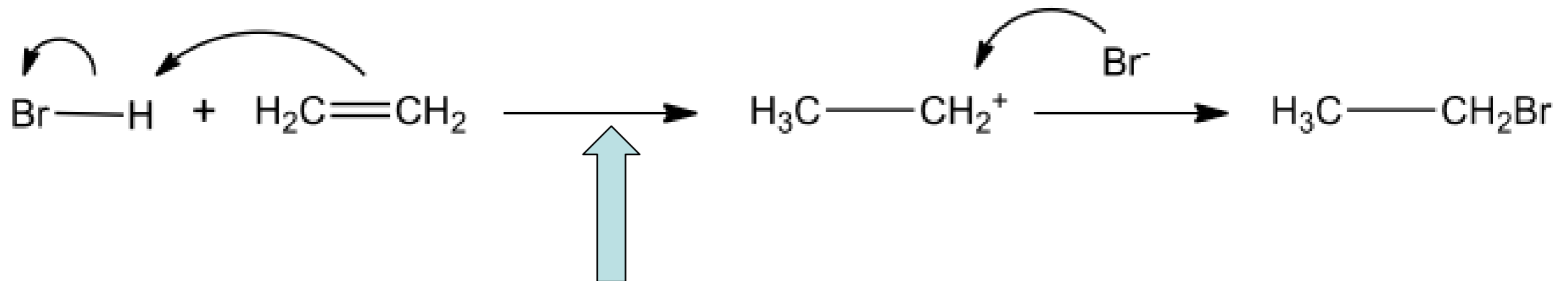
$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$$

$$\Delta G^\circ = -RT \ln K \quad \text{van 't Hoff equation is related to equilibrium}$$

Energy Diagrams



Energy Diagrams



Energy Diagrams

Complete energy diagram for the two-step reaction:

