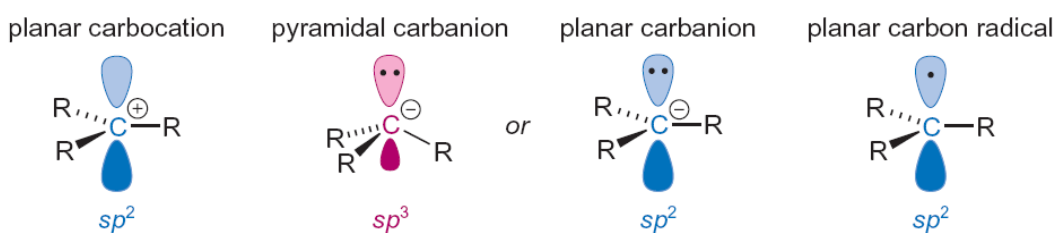


# Organic reaction mechanisms

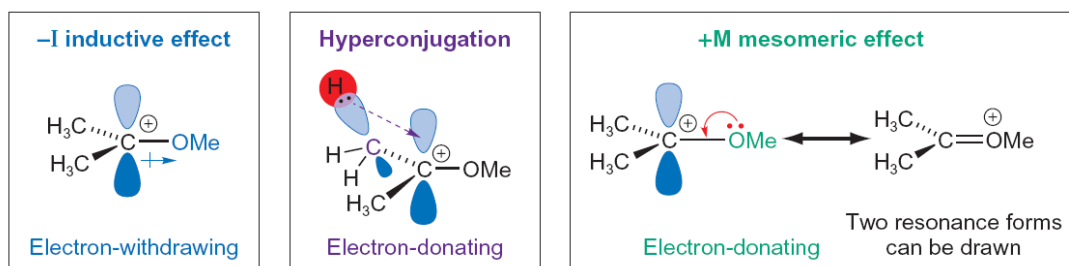
## 19.1 Fundamental concepts of organic reaction mechanisms

- Double-headed arrows are used to represent the movement of electrons in polar reactions.
- Single-headed arrows are used to represent the movement of electrons in radical reactions.
- Heterolytic cleavage (heterolysis) is the unsymmetrical cleavage of a covalent bond to form a cation and an anion.
- Homolytic cleavage (homolysis) is the symmetrical cleavage of a covalent bond to form two radicals.
- Short-lived carbocations, carbanions, and carbon radicals, which can often be detected (but not isolated) in polar and radical reactions, are called reactive intermediates.
- The shape of the reactive intermediate depends on the hybridization of the carbon atom carrying the charge or unpaired electron.



## Electronic effects

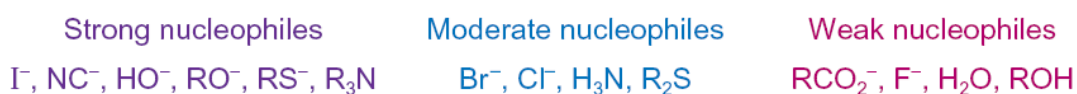
- Inductive effects and hyperconjugation refer to the polarization of electrons in  $\sigma$  bonds, while mesomeric effects refer to the delocalization of lone pairs of electrons and electrons in  $\sigma$  bonds.



- +I/+M groups are electron-donating groups that stabilize carbocations and –I/–M groups are electron-withdrawing groups that stabilize carbanions.
- A resonance hybrid is a molecule, ion, or radical that is a combination of a number of contributing resonance forms.
- Sometimes mesomeric and inductive effects work in the same direction, but more often they oppose one another.
- Mesomeric effects are generally stronger, and can be more effective over longer distances, than inductive effects and hyperconjugation.
- Conjugated molecules contain alternating single and double bonds.

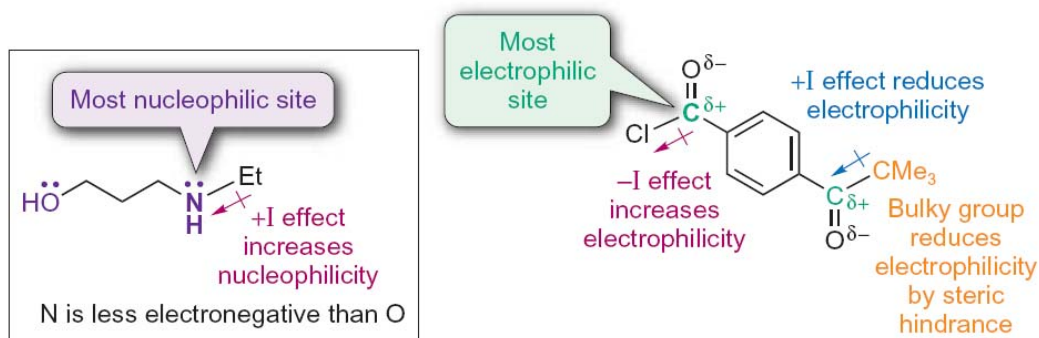
## Nucleophiles and electrophiles

- Nucleophiles are negatively charged ions or neutral molecules that *donate* a pair of electrons.
- Electrophiles are positively charged ions or neutral molecules that *accept* a pair of electrons.
- Strong nucleophiles are anions (of large atoms that are not highly electronegative) or neutral molecules containing a lone pair of electrons (on an atom that is not highly electronegative).



Approximate order in polar protic solvents—order depends on the solvent

- Strong electrophiles are carbocations or neutral molecules with carbon bonded to highly electronegative atoms.



## 19.2 Classification of organic reaction mechanisms

### Acid–base reactions

- Acidic compounds have low  $pK_a$  values and are good proton donors.
- The more stable the conjugate base, the stronger the acid.
- Organic acids generally contain O–H and N–H bonds; relatively strong acids also have –I and –M groups that stabilize the conjugate base.
- Alkynes are more acidic than alkenes or alkanes because the lone pair of electrons in the conjugate base is in an  $sp$  orbital.
- Basic compounds are good proton acceptors.
- A strong base has a relatively stable conjugate acid, with a high  $pK_a$  value.
- Organic bases generally have a formal negative charge or a lone pair of electrons on nitrogen or oxygen.
- Relatively strong organic bases have +I and +M groups that stabilize the conjugate acid.
- Relatively weak neutral organic bases have –I and –M groups.
- Pyridine is a much stronger base than pyrrole.
- Acid–base reactions are equilibrium reactions, and the position of the equilibrium depends on the  $pK_a$  values of the acid and the conjugate acid of the base.

- For an acid to donate a proton to a base, the acid must have a lower  $pK_a$  value than the conjugate acid of the base.
- Acids and bases are useful catalysts. They can alter the reactivity of some organic molecules and increase the rate of reaction.

## Redox reactions

- Carbon atoms at the *same* oxidation level are interconverted without oxidation or reduction.
- Carbon atoms at *different* oxidation levels are interconverted by oxidation or reduction.
- When carbon atoms increase oxidation level in a reaction, it is an oxidation reaction.
- When carbon atoms decrease oxidation level in a reaction, it is a reduction reaction.

## Polar reactions

- An addition reaction involves the addition of two reactants to form a single product.
- An elimination reaction is the opposite of an addition reaction, as one reactant molecule is converted into two products.
- A substitution reaction involves a functional group in a particular compound being replaced by another group
- Functional groups react by characteristic reaction mechanisms:

electrophilic addition	alkene
nucleophilic addition	aldehyde, ketone
elimination	halogenoalkane
nucleophilic substitution	halogenoalkane
nucleophilic acyl substitution	carboxylic acid derivatives
electrophilic substitution	benzene (and derivatives)

## Radical reactions

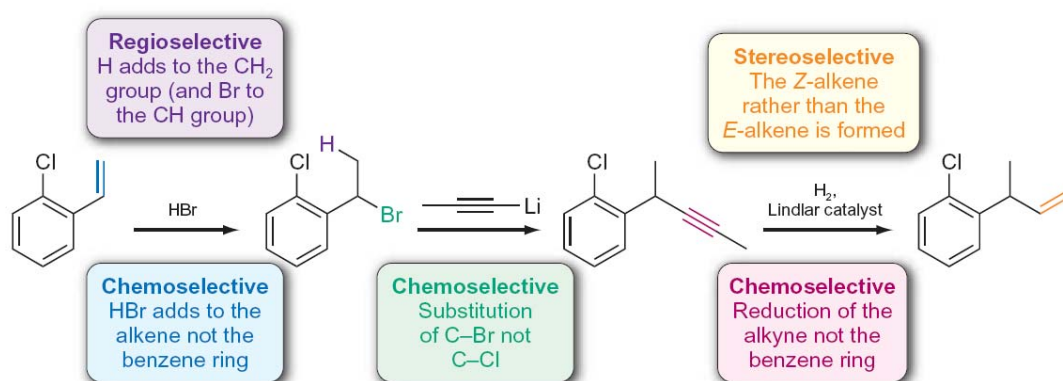
- An initiation step produces radicals that can react in chain reactions.
- Radical chain reactions are composed of a number of propagation steps. In a propagation step, a radical reactant forms a radical product.

- A termination step stops a radical chain reaction by converting radicals into non-radical products.

## Pericyclic reactions

### 19.3 Reaction selectivity

- A chemoselective reaction is a reaction in which one functional group reacts in preference to another functional group or groups.
- A regioselective reaction is a reaction that leads to the selective formation of one structural isomer.
- A stereoselective reaction is a reaction in which one enantiomer, one diastereomer, or one double bond isomer is formed selectively over others.



- In a stereospecific reaction, different stereoisomers react differently.

## Learning outcomes

By the end of this chapter you should be able to do the following.

- Use double-headed and single-headed arrows to represent the movement of electrons in polar and radical reactions, respectively.
- Recognize carbocations, carbanions, and carbon-centred radicals.
- Understand how hyperconjugation, inductive effects, and mesomeric effects affect the stability of ions and neutral organic molecules. Table 19.3 shows the inductive and mesomeric effects of some functional groups.

Table 19.3 Inductive and mesomeric effects of some functional groups. (Alkenes and aromatic rings can be +M or –M)

–I, –M groups*	–I, +M groups <sup>†</sup>	+I groups <sup>‡</sup>
–NO <sub>2</sub>	–OH	–R (alkyl)
–CO <sub>2</sub> H	–OR	–Li
–CO <sub>2</sub> R	–NH <sub>2</sub>	–MgBr
–COR	–NR <sub>2</sub>	
–CHO	–SR	
–CN	–Br	
	–Cl	

\* –I, –M groups contain an electronegative atom(s) and a double or triple bond.

<sup>†</sup> –I, +M groups contain an electronegative atom with a lone pair.

<sup>‡</sup> +I groups contain an electropositive atom or hydrocarbon chain.

- Recognize that steric effects can influence organic reactions.
- Recognize and compare the relative strengths of nucleophiles and electrophiles.
- Recognize the importance of orbital overlap in resonance and organic reactions.
- Draw sensible curly arrow mechanisms for reactions of nucleophiles with electrophiles.
- Recognize organic acids and the factors that influence acidic strength.
- Recognize organic bases and the factors that influence basic strength.
- Recognize acid–base reactions involving organic compounds.
- Classify functional groups by their oxidation level and use oxidation levels to recognize redox reactions.
- Classify polar reactions as electrophilic additions, nucleophilic additions, eliminations, nucleophilic substitutions, nucleophilic acyl substitutions, or electrophilic substitutions.
- Recognize radical initiation, propagation, and termination reactions.
- Recognize the Diels–Alder reaction as an example of a pericyclic reaction.
- Recognize chemoselective, regioselective, stereoselective, and stereospecific reactions.