CARBON CARBON EVERYWHERE!!

Macromolecules

(a) Some of the amino acids of proteins

- Alanine
- Serine
- Aspartate
- Cysteine
- Tyrosine
- Histidine

The parent sugar

α-D-Glucose

The components of nucleic acids

- Uracil
- Thymine
- Cytosine
- Adenine
- Guanine

Nitrogenous bases

- α-D-Ribose
- 2-Deoxy-α-D-ribose

Five Carbon sugars

Some components of lipids

- Choline
- Palmitate
- Oleate
- Cholesteryl
- Cholesterol
- Glycerol
- α-cholesterol

Phosphoric acid
Importance of carbon

- Single bond with Oxygen: \( \cdot \text{C} \cdot + \cdot \text{O} : \rightarrow \cdot \text{C} : \text{O} \)
- Single bond with Nitrogen: \( \cdot \text{C} \cdot + \cdot \text{N} : \rightarrow \cdot \text{C} : \text{N} \)
- Single bond with Carbon: \( \cdot \text{C} \cdot + \cdot \text{C} \cdot \rightarrow \cdot \text{C} : \text{C} \)

- Double bond with Oxygen: \( \cdot \text{C} \cdot + \cdot \text{O} \cdot \rightarrow \cdot \text{C} \cdot = \text{O} \)
- Double bond with Nitrogen: \( \cdot \text{C} \cdot + \cdot \text{N} \cdot \rightarrow \cdot \text{C} \cdot = \text{N} \)
- Double bond with Carbon: \( \cdot \text{C} \cdot + \cdot \text{C} \cdot \rightarrow \cdot \text{C} \cdot = \text{C} \)

- Triple bond with Carbon: \( \cdot \text{C} \cdot + \cdot \text{C} \cdot \rightarrow \cdot \text{C} \cdot \equiv \text{C} \)
Importance of carbon

- Methyl
- Phenyl
- Ethyl
- Amino
- Guanidino
- Sulfhydryl
- Amido
- Imidazole
- Disulfide
- Thioester
- Phosphoryl
- Phosphoanhydride
- Mixed anhydride
- Carbonyl (aldehyde)
- Ether
- Ester
- Carboxyl (ketone)
- Carboxyl
- Hydroxyl (alcohol)
- Anhydride

(carboxylic acid and phosphoric acid; also called acyl phosphate)

two carboxylic acids)
Importance of carbon

Acetyl-coenzyme A
Importance of carbon Geometry

Compounds of carbon can exist as **stereoisomers**

Stereoisomers -

Stereospecific - requires specific stereochemistry

Maleic acid (cis)  
Fumaric acid (trans)  

______________ isomers
Compounds of carbon can exist as **stereoisomers**

Stereoisomers - different molecules in which the order of bonding is the same, but the spatial relationship among the atoms is different - differing configuration

Stereospecific - requires specific stereochemistry

**geometric isomers**
Importance of geometry

HIV genome (gray) is made of RNA, it has a complementary surface for an important protein molecule to bind (colored stick model)
Importance of carbon

Chiral carbon

Chiral carbon -
**Importance of carbon**

**Chiral carbon**

Chiral carbon - asymmetric carbon with 4 different substituents
Molecules with chiral centers

\[ \text{L-Glyceraldehyde} \]
\[ \text{D-Glyceraldehyde} \]
\[ \text{L-Alanine} \]
\[ \text{D-Alanine} \]

19 of the 20 Amino acids in proteins have a chiral center.
**Importance of carbon**

**Chiral carbon**

In living organisms, chiral molecules usually exist in only one chiral form

Amino acids (protein building blocks) - only L isomers
Glucose (carbohydrate building block) - only D isomer

![Chemical structures](image)
Chemical reactivity

Five MAJOR reaction types in biochemistry

(1) Oxidation-Reduction Reactions

OXIDATION = Loss of electrons
REDUCTION = Gain of electrons

A dehydrogenation reaction - when a reactant loses 2 electrons and 2 H⁺ (enzyme = dehydrogenases) OXIDATION
Chemical reactivity

(2) Cleavage and formation of C-C bonds

Examples:

(a) \[ \text{O}^{\delta-} - C^{\delta+} - \]

(b) \[ \overset{\rightleftharpoons}{-C-C-} \rightarrow -C=\text{C} - \]

(c) \[ \overset{\rightleftharpoons}{R_1-C-C:} \overset{\text{H}^+}{\text{C}=\text{O}} \rightarrow R_1-C-C-C\text{-OH} \]

Aldol condensation

Claisen ester condensation

Decarboxylation of a $\beta$-keto acid
(2) Cleavage and formation of C-C bonds (or C-N bonds)
Monomeric subunits are joined with the release of water
Chemical reactivity

(2) Cleavage and formation of C-C bonds

\[ \overset{\text{Leaving Group}}{\text{C:W}} + \overset{\text{Nucleophile}}{\text{Z:}} \rightleftharpoons \text{C:Z} + \overset{\text{W:}}{\text{ }} \]

### Table 3-4

<table>
<thead>
<tr>
<th>Some Functional Groups Active as Nucleophiles within Cells*</th>
<th>Nucleophiles - rich in electrons</th>
<th>Electrophiles - electron deficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>HOH</td>
<td></td>
</tr>
<tr>
<td>Hydroxide ion</td>
<td>HO^-</td>
<td></td>
</tr>
<tr>
<td>Hydroxyl (alcohol)</td>
<td>ROH</td>
<td></td>
</tr>
<tr>
<td>Alkoxy</td>
<td>RO^-</td>
<td></td>
</tr>
<tr>
<td>Sulphydry</td>
<td>RSH</td>
<td></td>
</tr>
<tr>
<td>Sulfide</td>
<td>RS^-</td>
<td></td>
</tr>
<tr>
<td>Amino</td>
<td>RNH2</td>
<td></td>
</tr>
<tr>
<td>Carboxylate</td>
<td>R-CO^-</td>
<td></td>
</tr>
<tr>
<td>Imidazole</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Inorganic orthophosphate</td>
<td>O-P-OH</td>
<td></td>
</tr>
</tbody>
</table>

*Listed in order of decreasing strength. Weaker nucleophiles make better leaving groups.
Chemical reactivity

(2) Cleavage and formation of C-C bonds

Nucleophilic substitution - electron-rich group replaces departing anion

(a) Sn1 reaction

Substitution nucleophilic, unimolecular

(b) Sn2 reaction

Substitution nucleophilic, bimolecular
Chemical reactivity

(3) Internal rearrangements, isomerizations and eliminations

Redistribution of electrons results in
(i) isomerization
(ii) transposition of double bonds
(iii) cis-trans rearrangements of double bonds

(a) Glucose 6-phosphate \[\rightleftharpoons\] Fructose 6-phosphate by phosphohexose isomerase

(b) 1. $B_1$ abstracts a proton.
2. This allows the formation of a $C \equiv C$ double bond.
3. Electrons from carbonyl form an $O \equiv H$ bond with the hydrogen ion donated by $B_2$.
4. $B_2$ abstracts a proton, allowing the formation of a $C \equiv O$ bond.
5. An electron leaves the $C \equiv C$ bond to form a $C \equiv H$ bond with the proton donated by $B_1$.

Enediol intermediate
Chemical reactivity

(4) Group Transfers
In metabolism - attachment of a good leaving group to a metabolic intermediate to “activate” it for subsequent reaction

Good leaving group

Example

Adenine - Ribose

\[ \text{H}_{\text{O}} - \text{R} \]

Glucose

ATP

\[ \text{O} - \text{P} - \text{O} - \text{P} - \text{O} - \text{P} - \text{O}^{-} \]

ADP

\[ \text{O} - \text{P} - \text{O} - \text{P} - \text{O}^{-} + \text{O} - \text{P} - \text{O} - \text{R} \]

Glucose 6-phosphate, a phosphate ester
Chemical reactivity

(5) Free radical reactions
Homolytic cleavage of covalent bonds to generate free radicals

Repair of damaged DNA by DNA photolyase