I. DEFINITION & NOMENCLATURE OF ALDEHYDES & KETONES (19.1)

A. ALDEHYDES
   1. An aldehyde contains a carbonyl group and that bears a C and a H atom on the carbon atom of the carbonyl.
   2. NOMENCLATURE: Aldehydes are named in the following way:
      a. The parent name is based on the longest carbon chain that contains the carbonyl group.
      b. The parent name includes the carbon atom of the carbonyl group.
      c. The -CHO carbon atom is the #1 atom.
      d. The suffix used is "al". With two aldehyde functionalities it is "dial", with three "trial" etc...
      e. When the CHO- is a substituent, it is named as a "formyl" group.

B. KETONES
   1. A ketone contains a carbonyl group and that bears two carbon atoms on the carbon atom of the carbonyl.
   2. NOMENCLATURE: Ketones are named in the following way.
      a. The parent name is based on the longest carbon chain that contains the carbonyl group.
      b. The parent name includes the carbon atom of the carbonyl group.
      c. Numbering of the parent begins at the end of the carbon chain closest to the carbonyl group.
      d. The suffix used is "one". With two ketone functionalities it is "dione", with three "trione" etc...

C. RELATIVE REACTIVITIES OF CARBONYL COMPOUNDS WITH NUCLEOPHILES (Section 18.2)
   1. STERIC EFFECTS
      Steric effects influence the reactivity of the electrophilic carbonyl carbon in nucleophilic acyl addition and nucleophilic acyl substitution reactions. Carbonyl groups bonded to large, bulky substituents (eg., tertiary carbons) react slower with nucleophiles than carbonyl groups with smaller, less bulky substituents.
   2. ELECTRONIC EFFECTS
      Electronic effects influence the reactivity of the electrophilic carbonyl carbon in nucleophilic acyl addition and nucleophilic acyl substitution reactions. Substituents with lone pair electrons associated with them can donate electrons into the pi system, making the electrophilic carbonyl carbon less positive and less reactive with a nucleophile. Carbonyl-containing functional groups like carboxylic acids, esters and amides that have substituents with lone pairs (O or N atoms) react slower than aldehydes and ketones due to this electronic effect.

II. PREPARATION OF ALDEHYDES & KETONES (19.2)

A. ALDEHYDES: There are four basic methods for preparing aldehydes.
   1. OXIDATION OF 1° ALCOHOLS WITH PCC
   2. OZONOLYSIS OF ALKENES
   3. REDUCTION OF ESTERS
   4. HYDRATION OF TERMINAL ALKYNES WITH BH₃, H₂O₂, HO⁻

B. KETONES: There are five basic methods for preparing ketones.
   1. OXIDATION OF 2° ALCOHOLS
   2. OZONOLYSIS OF ALKENES
   3. FRIEDEL-CRAFTS ACYLATION
   4. HYDRATION OF TERMINAL ALKYNES WITH HgX₂, H₂O
   5. REACTION OF ACYL CHLORIDES WITH GILMAN REAGENTS

III. REACTIONS OF ALDEHYDES & KETONES:

A. NUCLEOPHILIC ADDITION REACTIONS (19.4)
   Aldehydes and ketones react with nucleophiles via the nucleophilic acyl addition reaction either under basic conditions or acidic conditions.

   Base-Catalyzed Nu: Acyl Addition

   ![Chemical Structure](Image)

   \[ R' = H \text{ aldehyde} \]
   \[ R \rightleftharpoons C \text{ ketone} \]
Acid-Catalyzed Nu: Acyl Addition

\[ O \]
\[ R \quad R' \quad \text{Oxonium Ion} \]
\[ \text{Nu:} \]
\[ \text{R' = H} \quad \text{aldehyde} \]
\[ R' = C \quad \text{ketone} \]

B. STEREOCHEMISTRY OF Nu ACYL ADDITIONS

1. Prochiral carbonyl carbons are carbons that when reacted with a nucleophile result in the formation of a new chiral center.

2. The carbonyl group has a trigonal planar geometry. The two sides of the carbonyl group (front and back) are referred to as “faces”. When the priorities of three substituents of the carbonyl group are oriented in a clockwise fashion (highest -> lowest), front face is called the Re face and the back face is referred to as the Si face.

3. Nucleophiles may attack carbonyl groups from the Re face or the Si face. The stereochemistry of the product depends on the priorities of the substituents and the priority of the nucleophile.
C. REACTIONS WITH SPECIFIC NUCLEOPHILES

1. ADDITION OF H_2O (19.5)

The addition of water to an aldehyde or ketone occurs either under acid or base catalysis.

a. Addition of water to a ketone or aldehyde in either acid or base, results in formation of a "gem diol".

b. The mechanism is different for acid and base catalyzed addition of water to an aldehyde or ketone.

c. Generally, the reaction is run in the presence of excess water.

2. ADDITION OF HCN (19.6)

Addition of HCN to an aldehyde or ketone results in formation of a cyanohydrin.
3. ADDITION OF ALCOHOLS (19.10)

- Addition of an alcohol to an aldehyde results in formation of an "acetal".
- Addition of an alcohol to a ketone results in formation of a "ketal".
- Generally, the reaction is run in the presence of excess alcohol.

4. ADDITION OF HYDRIDES (19.7)

- Sodium borohydride (NaBH₄) and lithium aluminum hydride (LiAlH₄) behave as an "H⁻" equivalent.
- LiAlH₄ is a stronger reducing agent than NaBH₄.

5. ADDITION OF AMINES & HYDRAZINES (19.8, 19.9)

- Amines
- Hydrazines
- Hydroxylamine

<table>
<thead>
<tr>
<th>Amines</th>
<th>Hydrazines</th>
<th>Hydroxylamine</th>
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</thead>
<tbody>
<tr>
<td>NH₂</td>
<td>H₂N-NH₂</td>
<td>H₂N-OH</td>
</tr>
<tr>
<td>N-H</td>
<td>H₂N-NH⁻R</td>
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</tbody>
</table>
1. Reaction of aldehydes and ketones with primary amines forms "imines".

2. Reaction of aldehydes and ketones with secondary amines forms "enamines" if an alpha-H is present.

3. Tertiary amines do not react with aldehydes and ketones.

4. Hydroxylamines react with aldehydes and ketones to give oximes.
4. Hydrazine and substituted hydrazines react with aldehydes and ketones to give hydrazones. If base is present (KOH) a reduction occurs to give an alkane. (Wolff-Kishner Reduction)

6. ADDITION OF GRIGNARD REAGENTS AND ALKYL LITHIUMS (19.7)

D. OXIDATIONS (19.3)
1. Aldehydes can be oxidized to carboxylic acids with Jones reagent (CrO₃, H₂SO₄) or with Tollens reagent (Ag₂O, NH₄OH, H₂O)

IV. CONJUGATE ADDITIONS TO α, β-UNSATURATED KETONES & ALDEHYDES
A. α,β-UNSATURATED CARBONYLs
1. α,β-Unsaturated carbonyls contain a carbonyl group in conjugation with a double bond. The four atoms of the α,β-unaturated system are designated 1-4 (as shown in figure below) and/or as the carbonyl carbon, carbonyl oxygen, the α-carbon and the β-carbon.

2. α,β-Unsaturated carbonyls react differently with some reagents than "simple" carbonyls. Specifically, some nucleophiles tend to react at the carbonyl carbon and some tend to react at the C₄ or β-carbon.
   a. Direct Additions (or 1,2 Additions)
      i. Direct additions between a α,β-unsaturated carbonyl and a nucleophile occurs at the carbonyl or C₂ carbon.
      ii. Grignard reagents, alkylolithiums (1, 2), and hydrides tend to react via a direct addition with α,β-unsaturated carbonyls
b. Conjugate or 1, 4-Additions
   i. Conjugate additions between a nucleophile and an α,β-unsaturated carbonyl occurs at the C₄ or β-carbon.
   ii. Enols and enolates, amines, nitriles, thiols and Gilman reagents tend to react with α,β-unsaturated carbonyls at the C₄ carbon.

Conjugate or 1, 4 Addition

\[ \text{E}^+ = H^+, R^+ (\text{from alkyl halide}) \text{ or carbonyl} \]

c. Steric crowding around the carbonyl carbon sometimes shifts the reaction for a direct addition to a conjugate addition.

B. CONJUGATE ADDITION OF GILMAN REAGENTS (DIALKYL CUPRULATE REAGENTS)
   1. Gilman reagents are formed upon reaction of two equivalents of an alkyl lithium reagent and cuprous iodide (CuI).
   2. Gilman reagents add to α,β-unsaturated carbonyls at the number "4" carbon atom.

C. CONJUGATE ADDITION WITH WATER

D. CONJUGATE ADDITION WITH AMINES