Aldehydes and Ketones

Aldehydes are compounds of the general formula HCHO; ketones are compounds of the general formula RR'CO. The groups R and R' may be aliphatic or aromatic.



Both aldehydes and ketones contain the carbonyl group, C O, and are often referred to collectively as carbonyl compounds. It is the carbonyl group that largely determines the chemistry of aldehydes and ketones.

This difference in structure affects their properties in two ways:

(a) aldehydes are quite easily oxidized, whereas ketones are oxidized only with difficulty;

(b) aldehydes are usually more reactive than ketones toward nucTeophilic addition, the characteristic reaction of carbonyl compounds.

structure of the carbonyl group

Carbonyl carbon is joined to three other atoms by a bonds; since these bonds utilize sp2 orbitals, they lie in a plane, and are 120 apart. The remaining/? orbital of the carbon overlaps a p orbital of oxygen to form a n bond; carbon and oxygen are thus joined by a double bond. The part of the molecule immediately surrounding carbonyl carbon is flat; oxygen, carbonyl carbon, and the two atoms directly attached to carbonyl carbon lie in a plane.



The electrons of the carbonyl double bond hold together atoms of quite different electronegativity, and hence the electrons are not equally shared; in particular, the mobile –n cloud is pulled strongly toward the more electronegative atom, oxygen.

The facts are consistent with the orbital picture of the carbonyl group. Electron diffraction and spectroscopic studies of aldehydes and ketones show that carbon, oxygen, and the two other atoms attached to carbonyl carbon lie in a plane; the three bond angles of carbon are very close to 120The large dipolc

moments of aldehydes and ketones indicate that the electrons or the carbonyl group arc quite unequally snared. We shall see how the physical and cfiemical properties of aldehydes and ketones are determined by the structure the carbonyl group.

<u>Nomenclature</u>

The common names of aldehydes are derived from the names of the corresponding carboxyiic acids by replacing -ic add by -aldehyde. The IUPAC names of aldehydes follow the usual pattern. The longest chain carrying the CHO group is considered the parent structure and is named by replacing the -e of the corresponding alkane by -al. The position of a substituent is indicated by a number, the carbonyl carbon always being considered as C-1. Here, as with the carboxylic acids, we notice that C-2 of the IUPAC name corresponds to alpha of the common name.



The simplest aliphatic ketone has the common name of acetone. For most other aliphatic ketones we name the two groups that are attached to carbonyl carbon, and follow these names by the word ketone. A ketone in which the carbonyl group is attached to a benzene ring is named as a -phenone, as illustrated below.

According to the IUPAC system, the longest chain carrying the carbonyl group is considered the parent structure, and is named by replacing the -e of the corresponding alkane with -one. The positions of various groups are indicated by numbers, the carbonyl carbon being given the lowest possible number.

Acetone Propanone

Methyl ethyl ketone Butanone

Ethyl ketone 3-Pentanone

CH₃ CH₃CH СНз

Methyl isopropyl ketone 3-Methyl-2-butanone

CH

r⊘

Benzophenone

Acetophenone

n-Butyrophenone

NO₂

3-Nitro-4.'-methylbenzophenone

Physical properties

1-The polar carbonyl group makes aldehydes and ketones polar compounds.

2- they have higher Boiling pOlliU lliaa aon-pulai compounds or comparable molecular weight.

3- they are not d&pable Of intermoiecular hydrogen bonding since they conten hydrogen bonded bfaiy to carbon; as a result they have lower boiling points than comparable alcohols or carboxylic acids.

4-The lower aldehydes and ketones are appreciably soluble in water, presumably because of hydrogen bonding between solute and solvent molecules; borderline solubility is reached at about five carbons .

5-Aldehydes and ketones are soluble in the usual organic solvents.

CH₃CH₂CH₂-C-CH₃

Methyl n-propyl ketone 2-Pentanone

Benzyl methyl ketone

1-Phenyl-2-propanone

PREPARATION OF ALDEHYDES

1. Oxidation of primary alcohols

	`	Ч
RCH₂OH	K ₂ Cr ₂ O ₇	R-C=0
1° Alcohol		Aldehyde

...

Example:

 $\begin{array}{cccc} CH_{3}CH_{2}CH_{2}CH_{2}OH & \xrightarrow{K_{2}Cr_{2}O_{7}, H_{2}SO_{4}, warm} & CH_{3}CH_{2}CH_{2}CHO \\ \hline n-Butyl alcohol & n-Butyraldehyde \\ (1-Butanol) & (Butanal) \\ B.p. 118^{\circ} & B.p. 76^{\circ} \end{array}$

2. Oxidation of methylbenzenes.



Examples:





3. Reduction of acid chlorides

RCOCl or ArCOCl LiAlH(Bu-t)₃→ RCHO or ArCHO Acid chloride Aldehyde

Examples:

LiAIH(Bu-r)3 сно p-Nitrobenzoyl chloride p-Nitrobenzaldehyde

4. Reimer-Tiemann reaction. Phenolic aldehydes.



PREPARATION OF KETONES

1. Oxidation of secondary alcohols



Example:



2. Friedel-Crafts acylation



Examples:

$$n-C_{5}H_{11}COCl + \bigotimes \xrightarrow{AlCl_{3}} n-C_{5}H_{11} - C - \bigotimes + HCl$$
Caproyl chloride

n-Pentyl phenyl ketone No rearrangement of n-pentyl group



4. Acetoacetic ester synthesis

Depending upon the availability of starting materials, aliphatic aldehydes can be prepared from alcohols or acid chlorides of the same carbon skeleton, and aromatic aldehydes can be prepared from methylbenzenes or aromatic acid chlorides.



Aliphatic ketones are readily prepared from the corresponding secondary alcohols, if these are available. More complicated aliphatic ketones can be prepared by the reaction of acid chlorides with organocadmium compounds.



Aromatic ketones containing a carbonyl group attached directly to an aromatic ring are conveniently prepared by Friedel-Crafjts acylation



The most likely mechanism for Friedel-Crafts acylation is analogous to the carbonium ion mechanism for Friedel-Crafts alkylation and involves the following steps:



Reactions. Nucleophilic addition

The carbonyl group, C=O, governs the chemistry of aldehydes and ketones. It does this in two ways: (a) by providing a site for nucleophilic addition, and

(b) by increasing the acidity of the hydrogen atoms attached to the alpha carbon.

What kind of reagents will attack such a group? Since the important step in these reactions is the formation of a bond to the electron-deficient (acidic) carbonyl carbon, the carbonyl group is most susceptible to attack by electron-rich, nucleophilic reagents, that is, by bases! The typical reaction of aldehydes and ketones is nucleophilic addition.

Nucleophilic addition





Trigonal

Reactant

state Becoming tetrahedral Partial negative charge on oxygen

Transition

Tetrahedral Negative charge H₂O

on oxygen

Product

REACTIONS OF ALDEHYDES AND KETONES

1. Oxidation.

(a) Aldehydes



Examples:

Tollens' $CH_{3}CHO + 2Ag(NH_{3})_{2}^{+} + 3OH^{-} \longrightarrow 2Ag + CH_{3}COO^{-} + 4NH_{3} + 2H_{2}O$ test Colorless Silver solution mirror

Tollens' reagent contains the silver ammonia ion, $Ag(NH_3)_2^+$. Oxidation of the aldehyde is accompanied by reduction of silver ion to free silver (in the form of a *mirror* under the proper conditions).

 $\begin{array}{ccc} \text{RCHO} + \text{Ag}(\text{NH}_3)_2^+ & \longrightarrow & \text{RCOO}^- + \text{Ag} \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & & \\ &$

(b) Methyl ketones

$$\begin{array}{cccc} \mathbf{R-C-CH_3} & \text{or} & \mathbf{Ar-C-CH_3} \xrightarrow{\mathbf{OX^-}} \mathbf{RCOO^-} & \text{or} & \mathbf{ArCOO^-} + \mathbf{CHX_3} & \begin{array}{c} Haloform\\ reaction \end{array} \end{array}$$

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Examples:

$$C_{2}H_{5}-C-CH_{3} + 3OI^{-} \longrightarrow C_{2}H_{5}COO^{-} + CHI_{3} + 2OH^{-}$$

Iodoform
Yellow; m.p. 119°

(4-Methyl-3-penten-2-one)

2. Reduction

(a) Reduction to alcohols.



(b) Reduction to hydrocarbons.



Clemmensen reduction for compounds sensitive to base

Wolff-Kishner reduction for compounds sensitive to acid

Examples ·



(c) Reductive animation.



3. Addition of Grignard reagents

The organic group, transferred with a pair of electrons from magnesium to carbonyl carbon, is a powerful nucleophile.

5. Addition of cyanide. Cyanohydrin formation

Examples:

Nucleophilic reagent 5. Addition of bisulfite.

Addition involves nucleophilic attack by bisulfite ion on carbonyl carbon, followed by attachment of a hydrogen ion to carbonyl oxygen:

6. Addition of derivatives of ammonia.

Examples:

7. Addition of alcohols. Acetal formation.

Example:

The reaction is carried out by allowing the aldehyde to stand with an excess of the anhydrous alcohol and a little anhydrous acid, usually hydrogen chloride. In the preparation of ethyl acetals the water is often removed as it is formed by means of the azeotrope of water, benzene, and ethyl alcohol

There is good evidence that in alcoholic solution an aldehyde exists in equilibrium with a compound called a **hemiacetal**:

$$\begin{array}{ccc} H & H \\ R'-C = O + ROH & \stackrel{H^+}{\longleftrightarrow} & R' & C - OR \\ & & OH \\ & & OH \\ & & A \text{ hemiacetal} \end{array}$$

A hemiacetal is formed by the addition of the nucleophilic alcohol molecule to the carbonyl group; it is both an ether and an alcohol. With a few exceptions, hemi-acetals are too unstable to be isolated.

In the presence of acid the hemiacetal, acting as an alcohol, reacts with more of the solvent alcohol to form the acetal, an ether:

$$\begin{array}{ccc} H & H \\ R'-C-OR + ROH & \stackrel{H^+}{\longleftrightarrow} & R'-C-OR + H_2O \\ OH & OR \\ Hemiacetal & Acetal \\ (An alcohol) & (An ether) \end{array}$$

The reaction involves the formation (step 1) of the ion I, which then combines (step 2) with a molecule of alcohol to yield the protonated acetal. As we can see,

Acetal formation thus involves :-

(a) nucleophilic addition to a carbonyl group, and

(b) ether formation via a carbonium ion.

(8) Cannizzaro reaction

In the presence of concentrated alkali, aldehydes containing no a-hydrogeris undergo selfoxidation-and-reduction to yield a mixture of an alcohol and a salt of a carboxylic acid. This reaction, known as the Cannizzaro reaction, is generally brought about by allowing the aldehyde to stand at room temperature with concentrated aqueous or alcoholic hydroxide.

9. Halogenation of ketones.

The kinetics is quite consistent with the following mechanism. The base

10. Addition of carbanions.

(a) Aldol condensation

Under the influence of dilute base or dilute acid, two molecules of an aldehyde or a ketone may combine to form a 0-hydroxyaldehyde or 0-hydroxyketone. This reaction is called the aklol condensation. In every case the product results from addition of one molecule of aldehyde (or ketone) to a second molecule in such a way"that the a-carbon of the first becomes attached to the carbonyl carbon of the second. For example:

If the aldehyde or ketone does not contain an α -hydrogen, a simple aldol condensation cannot take place. For example:

The generally accepted mechanism for the base-catalyzed condensation involves the following steps, acetaldehyde being used as an example. Hydroxide ion

(1) $CH_3CHO + OH^- \xrightarrow{\longrightarrow} H_2O + [CH_2CHO]^-$ Basic 1 catalyst

(b) Reactions related to aldol condensation

There are a large number of condensations that are closely related to the aldol condensation. Each of these reactions has its own name Perkin, Knoevenagel, Doebner, Claisen, Dieckmann, for example and at first glance each may seem quite different from the others. Closer examination shows, however, that like the aldol condensation each of these involves attack by a carbanion on a carbonyl group. In each case the carbanion is generated in very much the same way: the abstraction by base of a hydrogen ion alpha to a carbonyl group. Different bases may be used sodium hydroxide, sodium ethoxide, sodium acetate, amines and the carbonyl group to which the hydrogen is alpha may vary aldehyde, ketone, anhydride, ester but the chemistry is essentially the same as that of the aldol condensation.

(c) Wittig reaction

In 1954, Georg Wittig (then at the University of Ttibingcn) reported a method of synthesizing alkenes from carbonyl compounds, which amounts to the replace ment of carbonyl oxygen, O, by the group --CRR'. The heart of the synthesis

The preparation of ylides is a two-stage process, each stage of which belongs to a familiar reaction type: nucleophilic attack on an alkyl halide, and abstraction of a proton by a base.

Many different bases have been used—chiefly alkoxides and organometallics and in a variety of solvents. For example:

 $CH_{3}Br + Ph_{3}P \longrightarrow Ph_{3}P \xrightarrow{-CH_{3}}Br^{-} \xrightarrow{C_{6}H_{3}Li} Ph_{3}P = CH_{2} + C_{6}H_{6} + LiBr$ $CH_{2} = CHCH_{2}Cl + Ph_{3}P \longrightarrow Ph_{3}P \xrightarrow{-CH_{2}}CH_{2}CH = CH_{2}Cl^{-} \xrightarrow{N_{8}OEt}_{DMF}$ $Ph_{3}P = CHCH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}C$

is the nucleophilic attack on carbonyl carbon by an *ylide* to form a *betaine* which—often spontaneously—undergoes elimination to yield the product. For example:

 $(C_{6}H_{5})_{2}C = O + Ph_{3}P = CH_{2} \longrightarrow (C_{6}H_{5})_{2}C - CH_{2} \longrightarrow (C_{6}H_{5})_{2}C = CH_{2}$ Benzophenone Methylenetriphenylphosphorane $O PPh_{3} \qquad 1,1-Diphenylethene$

 $\begin{array}{cccc} C_6H_5CHO + C_6H_5CH = & CH - CH = PPh_3 & \longrightarrow & C_6H_5CH - CH - CH = & CHC_6H_5 & \longrightarrow \\ Benzaldehyde & & & \downarrow & \downarrow \\ & & & & O & PPh_3 \end{array}$

C₆H₅CH==CH--CH==CHC₆H₅ 1,4-Diphenyl-1,3-butadiene