ALDEHYDE & KETONE (Part-I)

By

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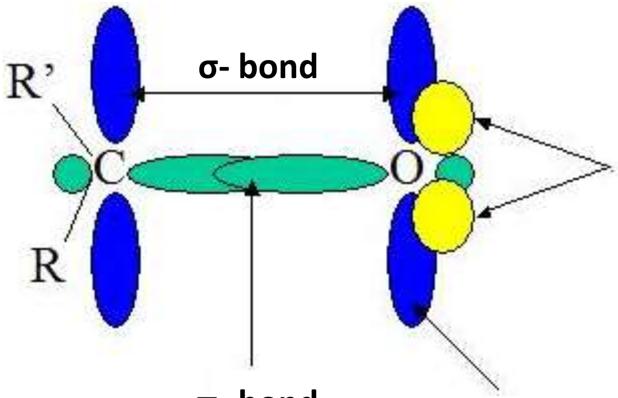
Structure of Aldehydes and Ketones

- The carbonyl carbon of an aldehyde or ketone is sp^2-hybridized.
- The bond angle is close to 120° (i.e. trigonal planar).
- The carbon-oxygen double bond consists of:

–σ C-O bond

– π C=O bond



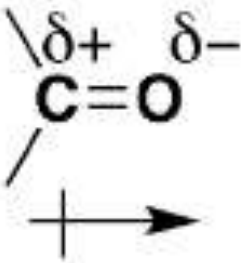
σ- bond

Lone electron pairs found in these orbitals

π- bond

p- orbital

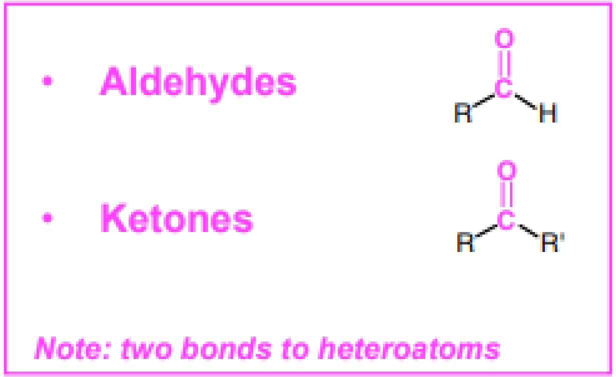
- Oxygen has two lone pairs of electrons hanging around. These electrons make the oxygen more electronegative than carbon.
- The carbon is then partially postive (electrophillic) and the oxygen partially negative (nucleophillic).



- The polarization of carbonyl groups also effects the boiling point of aldehydes and ketones to be higher than those of hydrocarbons.
- The double bond lengths of a carbonyl group is about 1.2 angstroms and the strength is about 176-179 kcal/mol).
- The length of a carbonyl bond is correlate with its polarity; the longer the bond, lower the polarity.
- The C=C is less reactive due to C=O electronegativity attributed to the oxygen and its two lone pairs of electrons.

Nomenclature of Aldehydes and Ketones

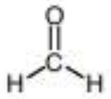
- Aldehydes and ketones are Carbonyl compounds containing the carbonyl group, **C=O**.



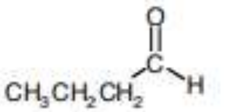
- **Aldehydes**
- **Ketones**

Note: two bonds to heteroatoms

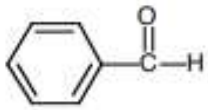
- Common names are used for the simplest aldehydes and ketones:



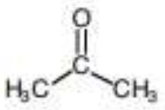
formaldehyde



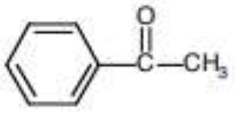
butyraldehyde



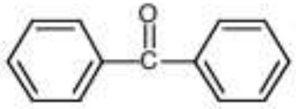
benzaldehyde



acetone

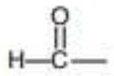


acetophenone



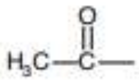
benzophenone

- Common names are also used for carbonyl-containing substituent groups, which are known collectively as acyl groups.



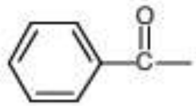
$H-\overset{\overset{O}{\|}}{C}-$

formyl



$H_3C-\overset{\overset{O}{\|}}{C}-$

acetyl

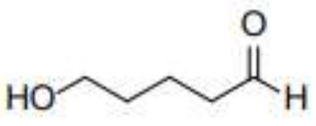


benzoyl

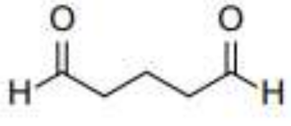
- In the IUPAC system, aldehydes and ketones are named according to the following procedure:

- The name of the parent hydrocarbon (alkane or alkene or alkyne) is determined while counting the carbonyl carbon as a methyl group for aldehydes and as a methylene group for ketones. The substituents are named as it is done for the hydrocarbon while considering the position of aldehyde as 1-position. For both aldehydes and ketones, the naming is done as in alkanes but keeping in mind the priority sequence and rule of lowest locants.

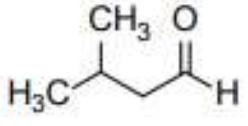
- The name of the alkane is modified to alkanal for an aldehyde. In case of ketones, the name is modified to alkanone. The position of the carbonyl group is denoted as numerical prefix to –one.



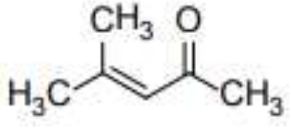
5-hydroxypentanal



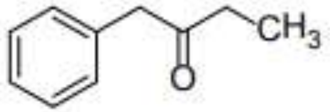
Pentan-1,5-dial



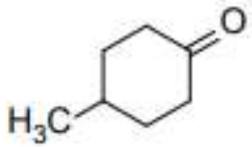
3-methylbutanal



4-methylpent-3-en-2-one

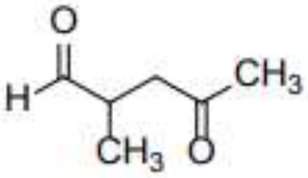


1-phenylbutan-2-one



4-methylcyclohexanone

- In cases where both the aldehyde and keto functionalities are present in the same molecule, the aldehyde gets preference and the molecule is suffixed with an –al. The position of the keto group is denoted by a numerical prefix and is denoted by used of the word oxo.

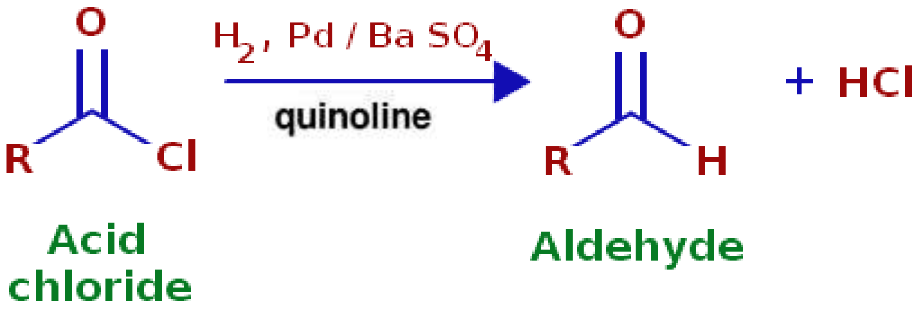


2-methyl-4-oxopentanal

Preparation of Aldehydes and Ketones

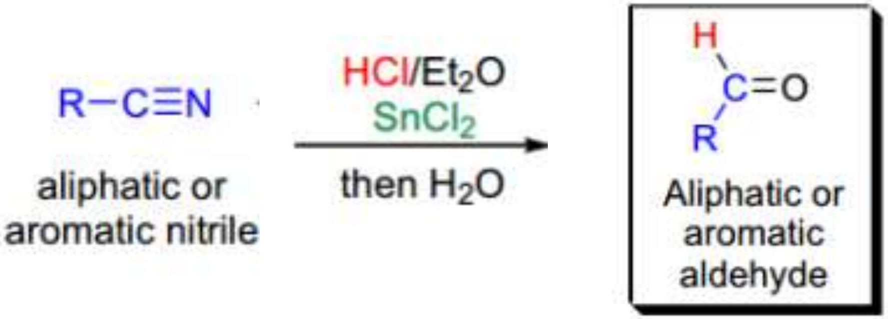
1) Reduction of Acid Chloride (Rosenmund reduction)

Rosenmund reduction is hydrogenation process in which an acyl chloride is selectively reduced to an aldehyde using a palladium catalyst suspended on barium sulphate. This process demonstrates the control of chemoselectivity by poisoning of the catalyst. The role of barium sulphate is to prevent the reaction from proceeding further to alcohol.



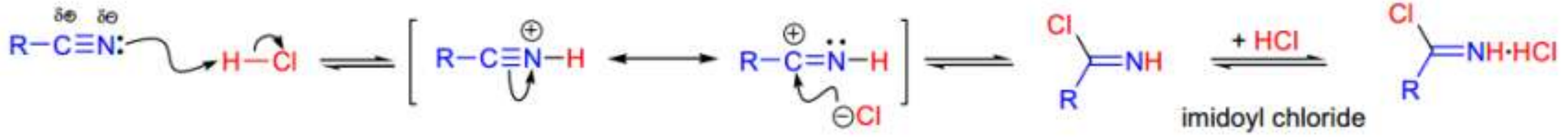
2) From Nitriles (Stephen reduction)

The reaction describes the preparation of aldehydes from **nitriles** with the help of tin(II) chloride and hydrochloric acid.

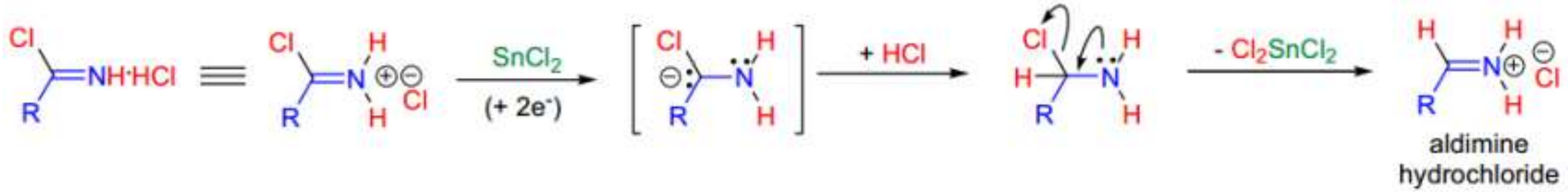


Mechanism

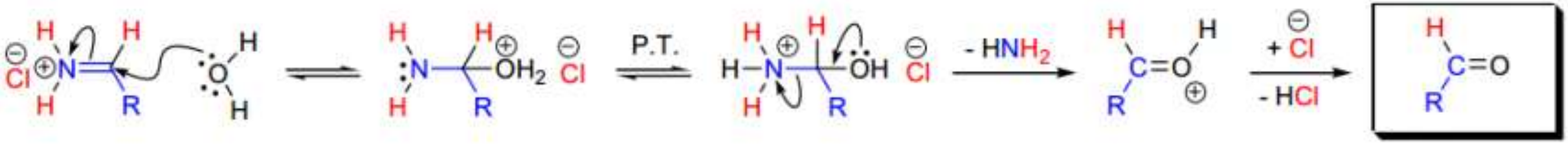
Step 1: Formation of the imidoyl chloride intermediate



Step 2: Reduction of the imidoyl chloride to the aldimine

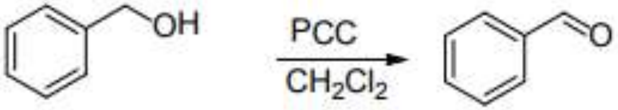


Step 3: Hydrolysis of the aldimine to the corresponding aldehyde with water:

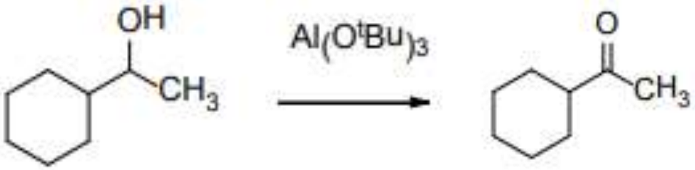


3) Oxidation of Alcohols

Aldehydes can be prepared from primary alcohols with the help of oxidizing agents such as pyridinium chlorochromate (PCC) and pyridiniumdichromate (PDC).

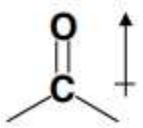


The ketones may also be generated from the secondary alcohols using aluminium *t*butoxide in the presence of acetone.



Physical properties of Aldehydes and Ketones

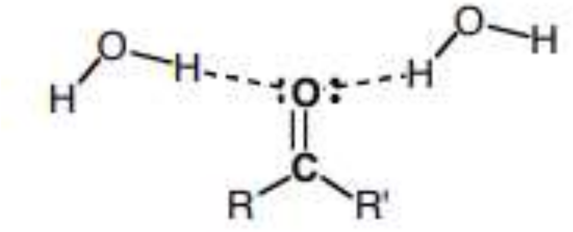
- Lower members of aldehydes have pungent odors and higher aldehydes have pleasant odors.
- Lower members of ketones have a pleasant odor, but most of the higher homologs have rather bland odors.
- Aldehydes and ketones are polar molecules because the C=O bond has a dipole moment:



For acetone: dipole moment = 2.7 D
boiling piint = 56.5 °C
For propene: dipole moment = 0.4 D
boiling point = -47.4 °C
For i-propanol: dipole moment = 1.7 D
boiling point = 82.3 °C

- Aldehydes and ketones are more polar than alkenes. So, have higher boiling points than alkenes of similar molecular weight.

- Aldehydes and ketones are not hydrogen bond donors (they can't donate a proton); therefore, they have lower boiling points than alcohols of similar molecular weight.



- Aldehydes and ketones are hydrogen bond acceptors; this makes them have considerable solubilities in water.
- Ketones such as acetone are good solvents because they dissolve both aqueous and organic compounds. Acetone is a polar, aprotic solvent.
- As the carbon chain increases in length, solubility in water decreases.
- All aldehydes and ketones are soluble in organic solvents and, in general, are less dense than water