Aldehydes and ketones

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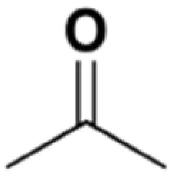
Aldehyde and ketone,

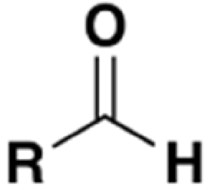
-Aldehydes and ketones contain the carbonyl group.

-Aldehydes contain the carbonyl group bonded to at least one hydrogen atom.

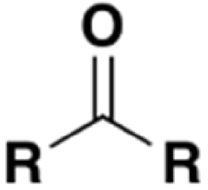
-Ketones contain the carbonyl group to two carbon atoms.



carbonyl group



aldehyde



ketone

- Aldehydes and ketones are organic compounds which incorporate a carbonyl functional group, C=O.
- The carbon atom of this group has two remaining bonds that may be occupied by hydrogen, alkyl or aryl substituents.
- If at least one of these substituents is hydrogen, the compound is an aldehyde. If neither is hydrogen, the compound is a ketone.

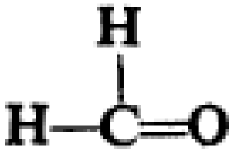
Nomenclature of aldehydes

The IUPAC names of aldehydes follow the usual pattern.

- The longest chain carrying the **CHO** group is considered the **parent structure.**
- Is named by replacing the **-e** of the corresponding alkane by **-al**.

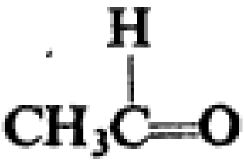
Nomenclature of aldehydes

- The position of a substituent is indicated by a number, the carbonyl carbon always being considered as C-1.
- C-2 of the IUPAC name corresponds to alpha of the common name.



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

Formaldehyde
Methanal

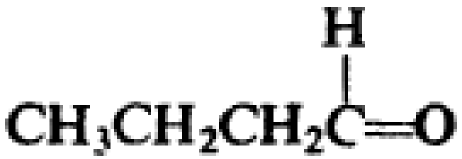


$$\mathrm{CH_3\overset{H}{\overset{|}{C}}=O}$$

Acetaldehyde
Ethanal

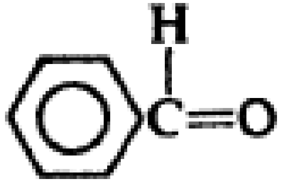
$$\mathrm{CH_3CH_2\overset{H}{\overset{|}{C}}=O}$$

Propionaldehyde
Propanal



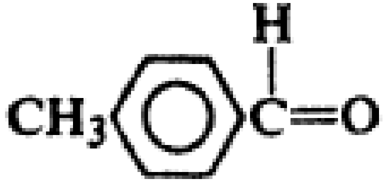
$$\mathrm{CH_3CH_2CH_2\overset{H}{\overset{|}{C}}=O}$$

n-Butyraldehyde
Butanal

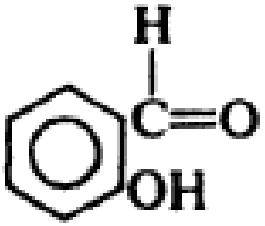


Benzaldehyde

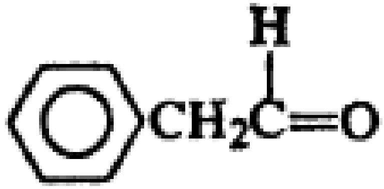
p-Nitrobenzaldehyde



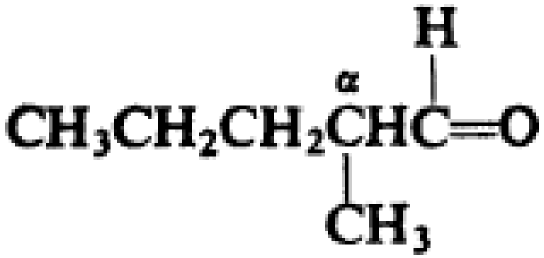
p-Tolualdehyde



Salicylaldehyde
(*o*-Hydroxybenzaldehyde)

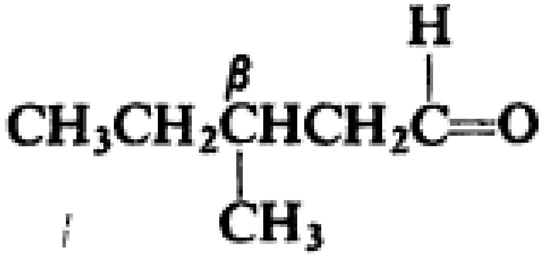


Phenylacetaldehyde
(Phenylethanal)



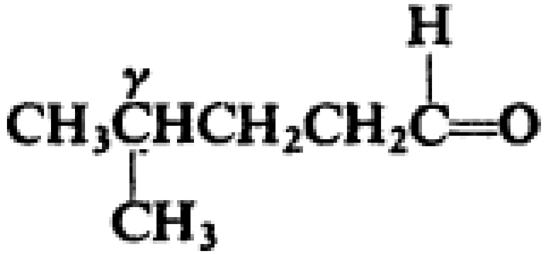
$\mathrm{CH_3CH_2CH_2}\underset{\mathrm{CH_3}}{\underset{|}{\overset{\alpha}{\mathrm{C}}}}\mathrm{H}\overset{\mathrm{H}}{\overset{|}{\mathrm{C}}}{=}\mathrm{O}$

α-Methylvaleraldehyde
2-Methylpentanal



$\mathrm{CH_3CH_2}\underset{\mathrm{CH_3}}{\underset{|}{\overset{\beta}{\mathrm{C}}}}\mathrm{HCH_2}\overset{\mathrm{H}}{\overset{|}{\mathrm{C}}}{=}\mathrm{O}$

β-Methylvaleraldehyde
3-Methylpentanal



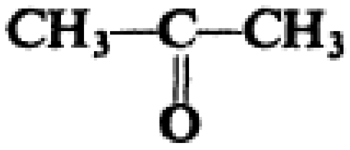
$\mathrm{CH_3}\underset{\mathrm{CH_3}}{\underset{|}{\overset{\gamma}{\mathrm{C}}}}\mathrm{HCH_2CH_2}\overset{\mathrm{H}}{\overset{|}{\mathrm{C}}}{=}\mathrm{O}$

Isocaproaldehyde
γ-Methylvaleraldehyde
4-Methylpentanal

Nomenclature of ketones

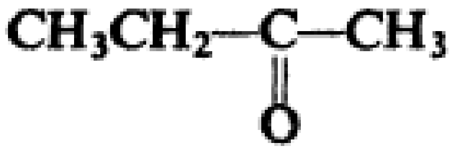
- The simplest aliphatic ketone has the common name of acetone.
- For aliphatic ketones we name the two groups that are attached to carbonyl carbon, and follow these names by the word ketone.
- A ketone in which the carbonyl group is attached to a benzene ring is named as a –**phenone**.

- 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.



$CH_3-\underset{\overset{\|}{O}}{C}-CH_3$

Acetone
Propanone

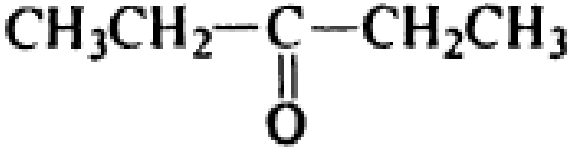


$CH_3CH_2-\underset{\overset{\|}{O}}{C}-CH_3$

Methyl ethyl ketone
Butanone

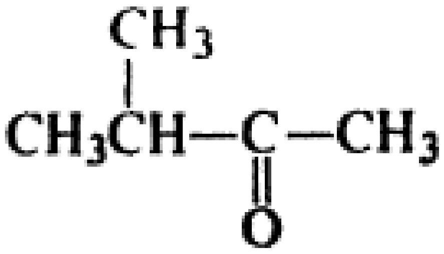
$CH_3CH_2CH_2-\underset{\overset{\|}{O}}{C}-CH_3$

Methyl *n*-propyl ketone
2-Pentanone



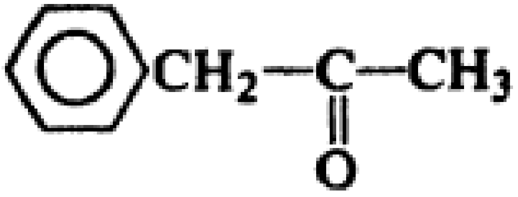
$CH_3CH_2-\underset{\overset{\|}{O}}{C}-CH_2CH_3$

Ethyl ketone
3-Pentanone

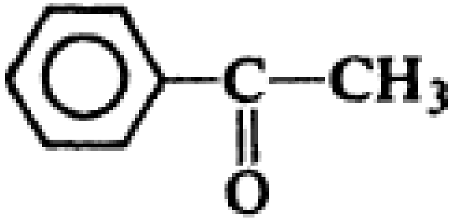


$CH_3\overset{\overset{CH_3}{|}}{C}H-\underset{\overset{\|}{O}}{C}-CH_3$

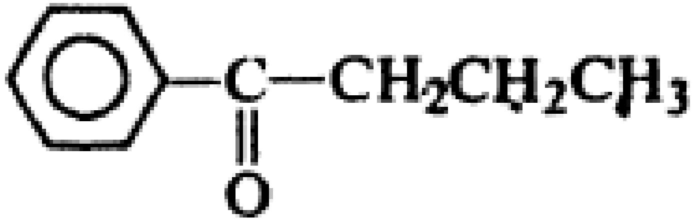
Methyl isopropyl ketone
3-Methyl-2-butanone



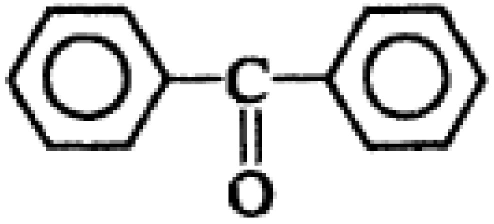
Benzyl methyl ketone
1-Phenyl-2-propanone



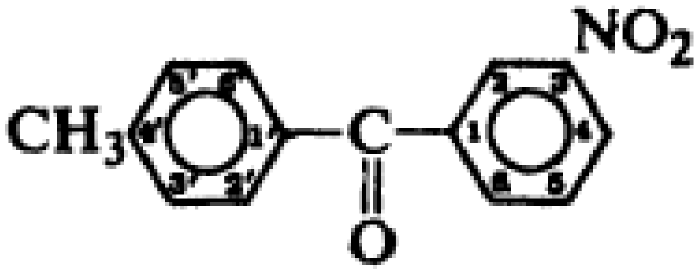
Acetophenone



n-Butyrophenone



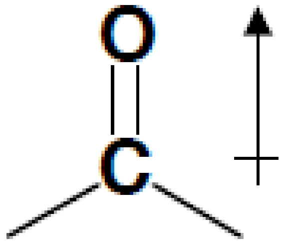
Benzophenone



3-Nitro-4'-methylbenzophenone

Physical properties

- Aldehydes and ketones are polar molecules because the C=O bond has a dipole moment:

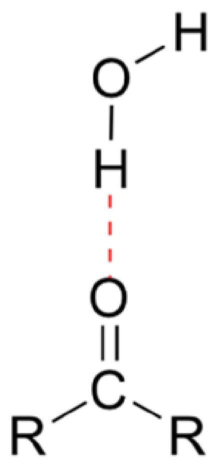


• Their polarity makes aldehydes and ketones have higher boiling points than alkenes of similar molecular weight.

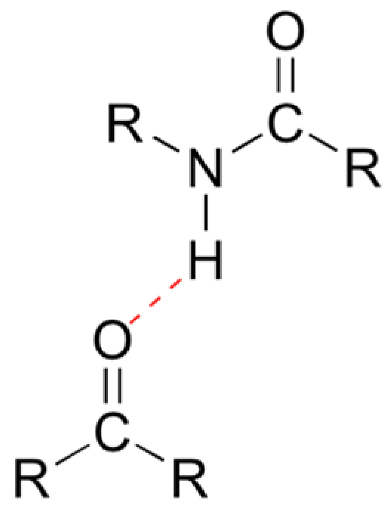
Physical properties

- 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 solubility in water.

- Ketones such as acetone are good solvents because they dissolve both aqueous and organic compounds. Recall that acetone is a ***polar, aprotic*** solvent.



hydrogen bonding between
a ketone (acceptor) and
water (donor)

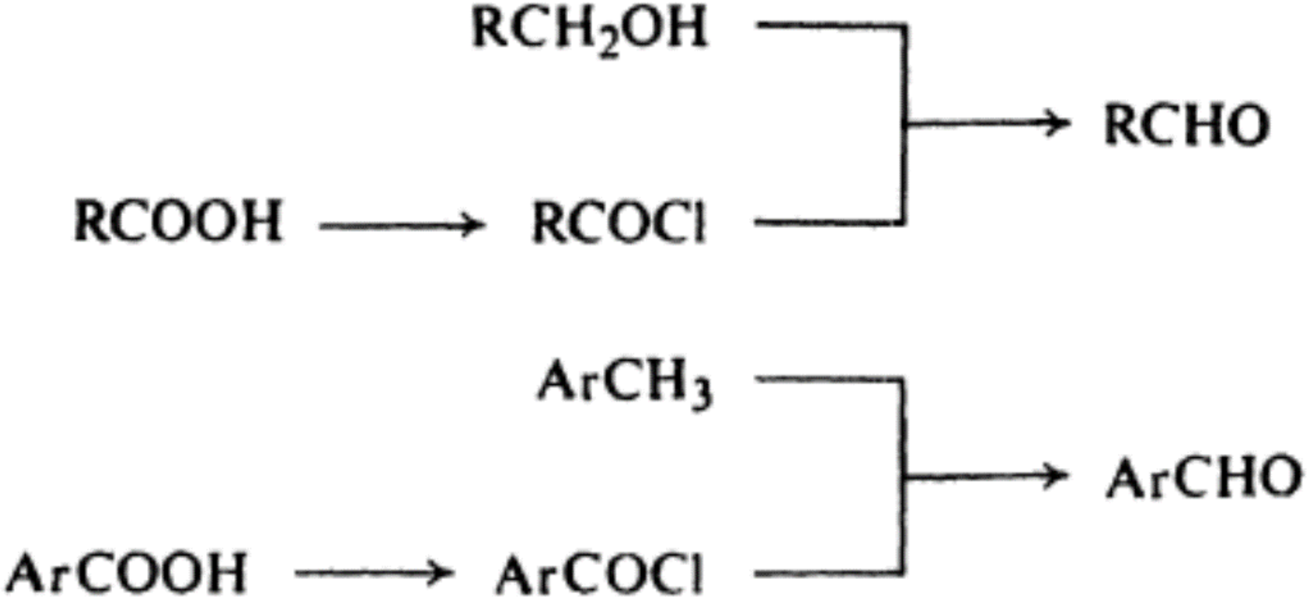


hydrogen bonding between
a ketone (acceptor) and an
amide (donor)

Preparation of aldehydes ketones

- Aliphatic aldehydes can be prepared from alcohols or acid chlorides of the same carbon skeleton.
- Aromatic aldehydes can be prepared from methylbenzenes or aromatic acid chlorides.

Preparation of aldehydes and ketones

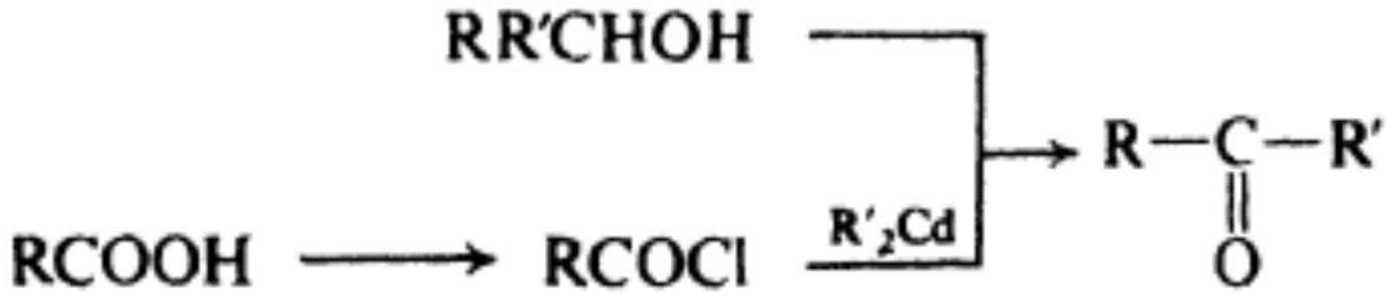


Preparation of aliphatic aldehydes

Preparation of aromatic aldehydes

Preparation of aldehydes and ketones

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



Preparation of aliphatic ketones

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

Preparation of aldehydes by oxidation methods

- Aldehydes are prepared by oxidation of corresponding primary alcohol using acidic dichromate (reagent).
- An aldehyde always has a lower boiling point than the alcohol from which it is formed.

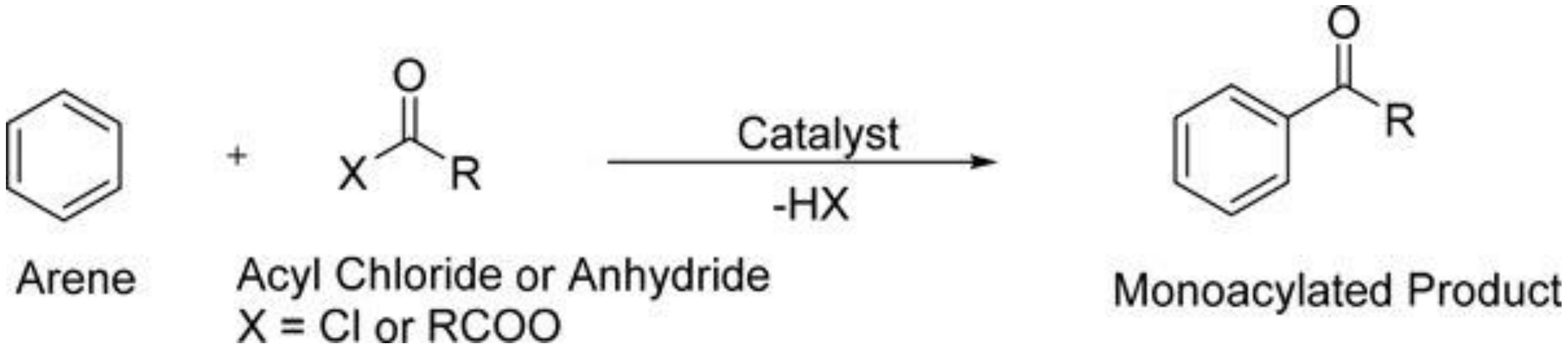
Preparation of aromatic ketones by Friedel-Crafts acylation

- A Friedel-Crafts reaction is an organic coupling reaction involving an electrophilic aromatic substitution that is used for the attachment of substituents to aromatic rings. The two primary types of Friedel-Crafts reactions are the alkylation and acylation reactions. These reactions were developed in the year 1877 by the French chemist Charles Friedel and the American chemist James Crafts.

Preparation of aromatic ketones by Friedel-Crafts acylation,

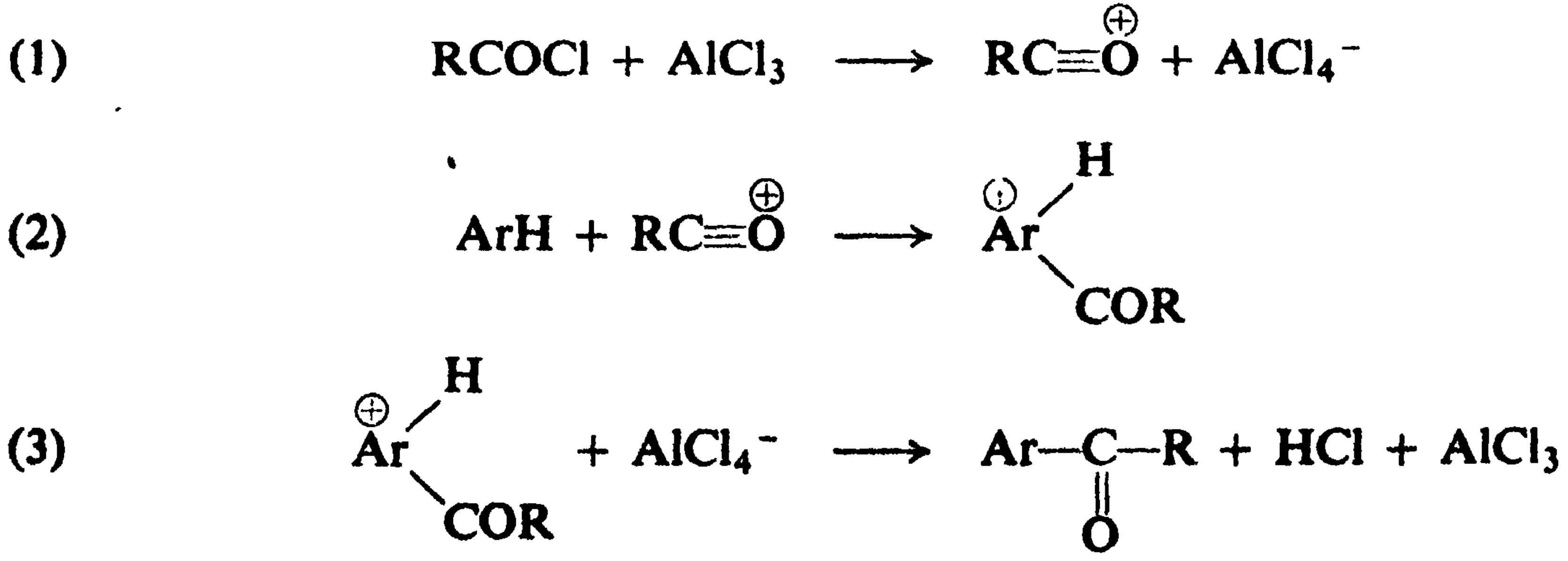
- An acyl group, **RCO** , becomes attached to the aromatic ring, thus forming a **ketone**; the process is called **acylation**.
- Catalysis by aluminium chloride (**AlCl3**) or another Lewis acid is required.

Preparation of aromatic ketones by Friedel-Crafts acylation:



Preparation of aromatic ketones by Friedel-Crafts acylation

- The mechanism for Friedel-Crafts acylation involves the following steps:



(1) $$RCOCl + AlCl_3 \longrightarrow RC\equiv\overset{\oplus}{O} + AlCl_4^-$$

(2) $$ArH + RC\equiv\overset{\oplus}{O} \longrightarrow \overset{\oplus}{Ar}\begin{matrix} H \\ COR \end{matrix}$$

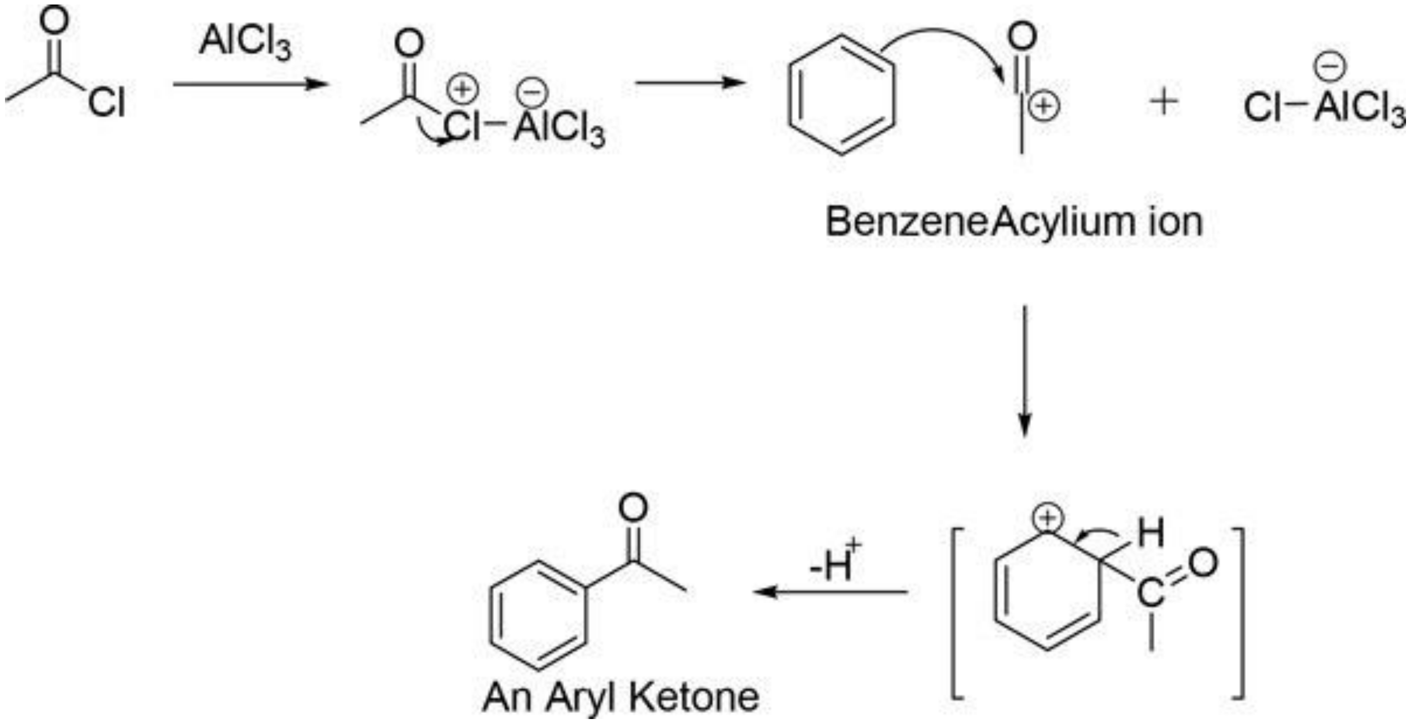
(3) $$\overset{\oplus}{Ar}\begin{matrix} H \\ COR \end{matrix} + AlCl_4^- \longrightarrow Ar-\underset{\underset{O}{\|}}{C}-R + HCl + AlCl_3$$

Detailed Mechanism of Frielel-Crafts acylation

- Friedel-Crafts acylation proceed through a four-step mechanism.

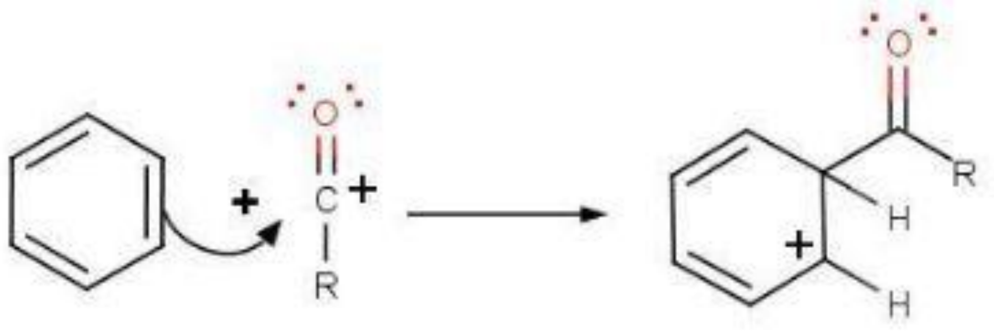
❖Step 1

- A reaction occurs between the Lewis acid catalyst ($AlCl_3$) and the acyl halide. A complex is formed and the acyl halide loses a halide ion, forming an acylium ion which is stabilized by resonance.


O
Cl
AlCl3
O
Cl
AlCl3
O
+
Cl
AlCl3
BenzeneAcylium ion
H
C
O
-H+
O
An Aryl Ketone

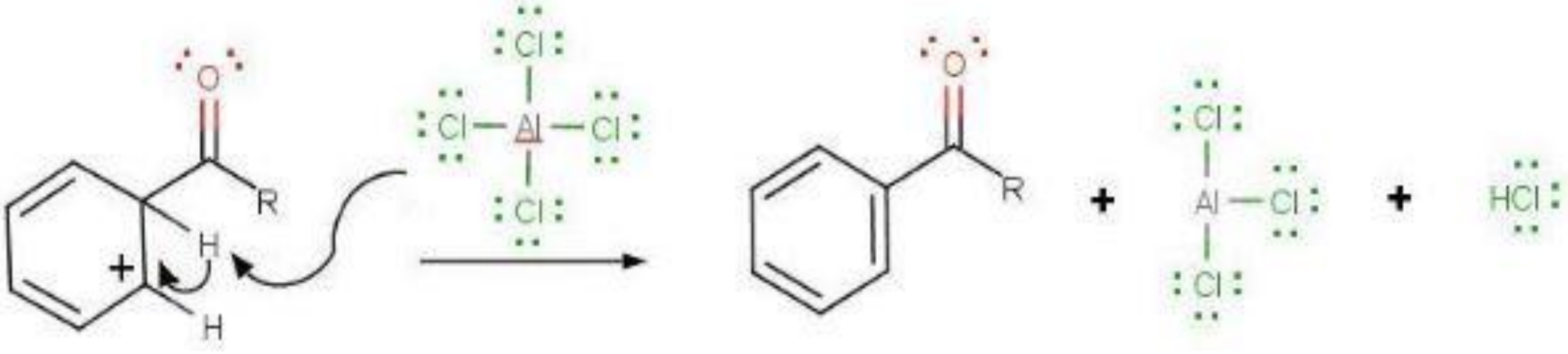
❖Step 2

- The acylium ion (RCO^+) goes on to execute an electrophilic attack on the aromatic ring. The aromaticity of the ring is temporarily lost as a complex is formed.



❖Step 3

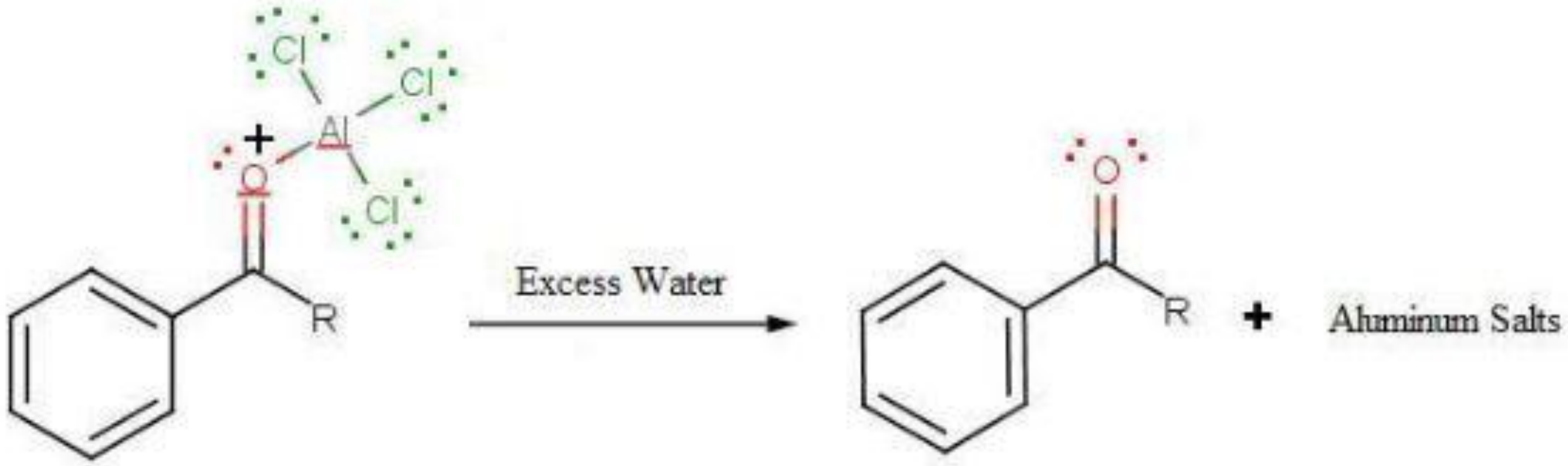
- The intermediate complex is now deprotonated, restoring the aromaticity to the ring. This proton attaches itself to a chloride ion (from the complexed Lewis acid), forming HCl. The $AlCl_3$ catalyst is now regenerated.



O
R
H
+
H
Cl
Cl
Al
Cl
Cl
O
R
+
Cl
Al
Cl
Cl
+
HCl

❖Step 4

- The regenerated catalyst can now attack the carbonyl oxygen. Therefore, the ketone product must be liberated by adding water to the products formed in step 3. This step can be illustrated as follows.


Cl
Cl
Cl
Al
+
O
R
Excess Water
O
R
+
Aluminum Salts

Thank you