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Department	Department of Higher Education, UT of Jammu and Kashmir
Class	Semester 3rd (UG-CBCS, General)
Paper	Organic Chemistry
Syllabus	➢ Carboxylic acids (aliphatic and aromatic) ➢ Preparation: Acidic and alkaline hydrolysis of esters ➢ Reactions: Hell-Vohlard-Zelinsky reaction

Carboxylic acids

Topic 1: Introduction of carboxylic acids

Topic 2: Nomenclature of carboxylic acids

Topic 3: Methods of preparation of carboxylic acids: Acid and alkaline hydrolysis of esters

Topic 4: Reactions of carboxylic acids: Hell-Volhard-Zelinsky reaction

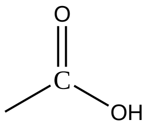
Learning objectives

To understand

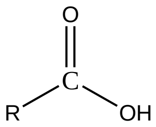
- Basics of carboxylic acids
- Nomenclature of carboxylic acids
- Methods of preparation of carboxylic acids
- Reactions of carboxylic acids

Topic1: Introduction of carboxylic acids

Carboxylic acids are the organic compounds which contain ***carboxyl*** functional group. Carboxyl group and carboxylic acid may be represented as



Carboxyl group

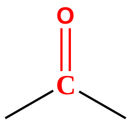


Carboxylic acid

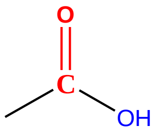
where -COOH is the carboxyl group

and R = Hydrogen or alkyl group or aryl group

Or we can say that when a ***carbonyl carbon*** (-CO-) also bears a ***hydroxyl group*** (-OH), then the resulting compounds are called ***carboxylic acids***.



Carbonyl group

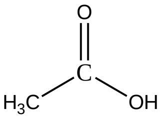


Carboxyl group

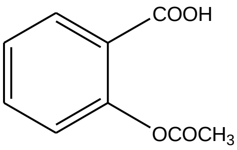
Interesting points to know about carboxylic acids:

1. Carboxylic acids occur widely in nature. Some carboxylic acids like acetic acid (CH_3COOH) have been known for the centuries. Carboxylic acids are present in many foods, medicines and household products. For example

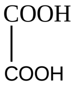
- ***Vinegar*** is made up of mostly water and ***acetic acid*** (CH_3COOH). In fact, characteristic odour and taste of vinegar is due to acetic acid.
- ***Aspirin*** is ***acetylsalicylic acid***
- ***Citrus fruits*** like lemons and oranges contain ***citric acid***. Citric acid gives these fruits sour or tart flavour
- ***Oxalic acid*** is present in ***spinach***



Acetic acid
(present in vinegar)

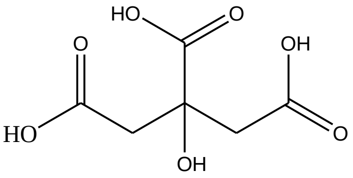


Acetylsalicylic acid
(Asprin)



$$\begin{array}{c} COOH \\ | \\ COOH \end{array}$$

Oxalic acid
(present in spinach)



Citric acid
(present in citrus fruits like lemons)

2. Acid chlorides, acid anhydrides, esters and amides are the derivatives of carboxylic acids. In other words, we can say that carboxylic acids are the parent compounds for these.

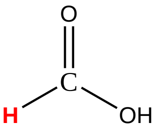
Classification of carboxylic acids:

Carboxylic acids are classified according to the substituent that is bonded to the carboxyl carbon. Depending on the substituent attached to the carboxyl group, carboxylic acids may be divided into following two categories:

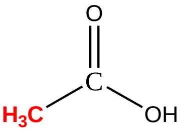
- Aliphatic carboxylic acids
- Aromatic carboxylic acids

Aliphatic carboxylic acids:

Aliphatic carboxylic acids have ***a hydrogen or an alkyl group*** bound to the carboxyl group. They may be represented as ***R-COOH*** where ***R=aliphatic group***. For example



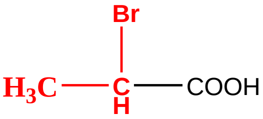
Formic acid
(Methanoic acid)



Acetic acid
(Ethanoic acid)

$H_2C{=}CHCOOH$

Acrylic acid
(Propenoic acid)



$$H_3C-\overset{Br}{\underset{H}{C}}-COOH$$

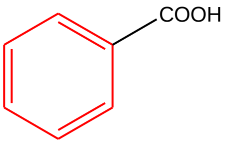
α-Bromopropionic acid

(2-Bromopropanoic acid)

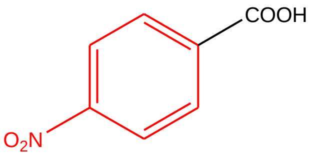
Note: Aliphatic is a term used for all compounds that are not aromatic. They may be saturated, unsaturated or even cyclic.

Aromatic carboxylic acids:

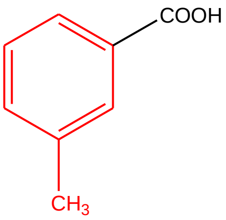
Aromatic carboxylic acids have an ***aryl group*** bound to the carboxyl group. They may be represented as **Ar**-***COOH*** where **Ar** = **aryl group**. For example



Benzoic acid



p-Nitrobenzoic acid



m-Toluic acid

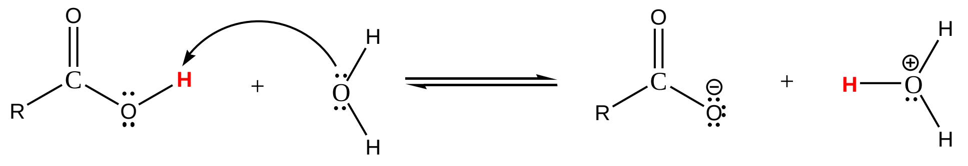
Note:

- ***The simplest carboxylic acid is formic acid.***
- *The* ***methylbenzoic acids*** *are given the special name of* ***toluic acids****.*

Acidity of carboxylic acids:

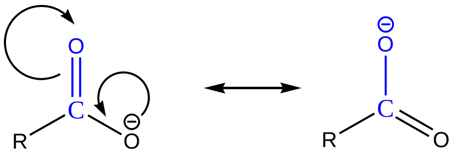
The most characteristic property of carboxylic acids is the one which gives them their name i.e. acidity. No doubt, ***carboxylic acids are weaker than mineral acids but they are the most acidic class of organic compounds that contain <u>only oxygen, carbon and hydrogen</u>.*** They are much stronger acids than alcohols and water.

A carboxylic acid **I** donates proton by the heterolytic cleavage of the O-H bond, generating a carboxylate anion **II**.



Carboxylic acid **I** Carboxylate anion **II**

The carboxylate anion **II** generated above is stabilised by resonance and moreover both the resonating structures (i.e. **II &III**) are exactly equivalent.



II **III**

Thus acidity of a carboxylic acid is because of the powerful resonance stabilization of carboxylate anion and this stabilization is possible only due to the presence of the carbonyl group **(-CO-).**

Topic 2: Nomenclature of carboxylic acids

Nomenclature of carboxylic acids can be discussed under two headings

- Common Nomenclature
- IUPAC nomenclature

Common Nomenclature:

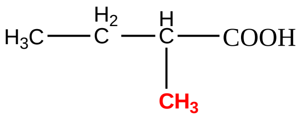
Carboxylic acids are a class of organic compounds which have been known for a long time. A large number of them are widely known by their common names. Their common names end with the suffix ***-ic acid*** and refer to ***their natural source rather than to their chemical structures.*** For example

- ***Formic acid*** was first obtained from ***red ants*** (Latin: ***formica means ant***)
- ***Acetic acid*** from ***vinegar*** (Latin: ***acetum means vinegar***)
- ***Butyric acid*** from ***rancid butter*** (Latin: ***butyrum means butter***)
- ***Caproic acid, caprylic acid*** and ***capric acid*** from ***goat fat*** (Latin: ***caper means goat***)

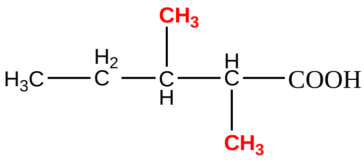
Branched chain carboxylic acids and substituted acids are named as derivatives of the straight chain acids. To indicate the position of the substituent, ***the Greek letters, α-, β-, γ-, δ- etc.*** are used. ***The α-carbon is the one bearing the carboxyl group***.

$$\mathbf{C}_{\delta}\text{-}\mathbf{C}_{\gamma}\text{-}\mathbf{C}_{\beta}\text{-}\mathbf{C}_{\alpha}\text{-}\mathrm{COOH}$$

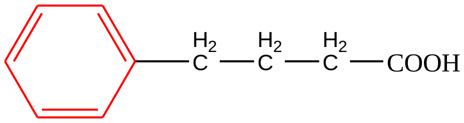
For example:



α-Methylbutyric acid

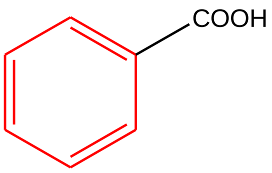


α,β-Dimethylvaleric acid

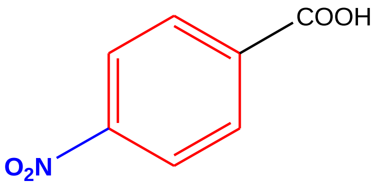


γ-Phenylbutyric acid

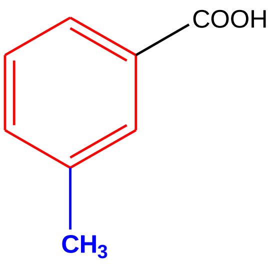
Aromatic acids are usually named as derivatives of benzoic acid.



Benzoic acid



p-Nitrobenzoic acid



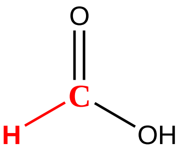
m-Toluic acid

Note: *The **methylbenzoic acids** are given the special name of **toluic acids**.*

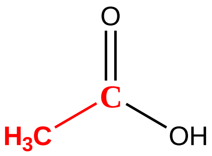
IUPAC nomenclature:

The IUPAC names follow the usual pattern. In IUPAC system, ***aliphatic carboxylic acids*** are named according to the following rules:

1. The ***longest continuous chain of carbons bearing the carboxyl group*** is considered as the ***parent structure*** and is named by ***replacing the -e of the corresponding alkane by -oic acid.***.



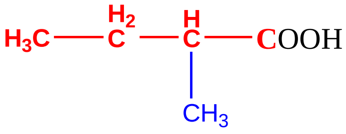
Methanoic acid



Ethanoic acid

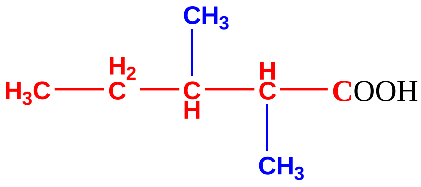
2. When substituents are present, their positions are indicated by number. ***The chain is numbered always starting with the carboxyl carbon atom.***

$$C_5\text{-}C_4\text{-}C_3\text{-}C_2\text{-}C_1OOH$$



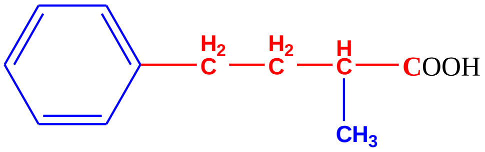
$H_3C-CH_2-CH(CH_3)-COOH$

2-Methylbutanoic acid



$H_3C-CH_2-CH(CH_3)-CH(CH_3)-COOH$

2,3-Dimethylpentanoic acid



2-Methyl-4-phenyl**butan**oic acid

3. Double bond in the main chain of the carboxylic acids is indicated using the suffix ***-enoic acid***. The chain is numbered starting with the carboxyl group, and ***a number designates the location of the multiple bond*** (and may include Z or E).

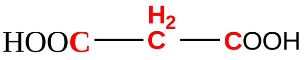
$H_2C{=}CHCOOH$

Propenoic acid

$H_2C{-}CH{=}CHCOOH$

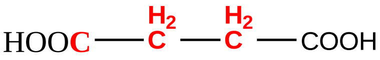
2-Butenoic acid

4. ***Aliphatic dicarboxylic acids*** are named by simply adding the suffix ***-dioic acid*** to the root name. The root name comes from the ***longest carbon chain containing both carboxyl groups***. ***The final -e in the name of the parent alkane is retained.***



$HOOC{-}CH_2{-}COOH$

Propanedioic acid

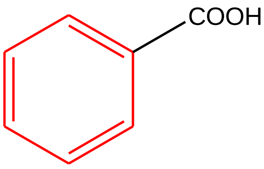


$HOOC{-}CH_2{-}CH_2{-}COOH$

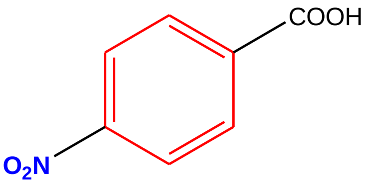
Butanedioic acid

Systematic names of aromatic carboxylic acids:

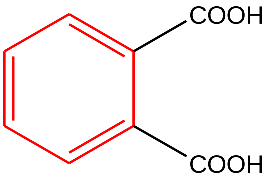
The systematic name of ***benzoic acid is benzenecarboxylic acid***. ***Other aromatic acids*** are usually named as ***derivatives of parent benzenecarboxylic acid***.



Benzenecarboxylic acid



4-Nitrobenzenecarboxylic acid



1,2-Benzenedicarboxylic acid

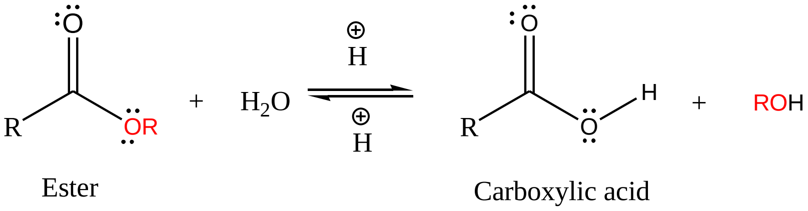
Topic 3: Methods of preparation of carboxylic acids: Acid and alkaline hydrolysis of esters

One of the methods for the preparation of carboxylic acids is the ***hydrolysis of esters***. Further, the hydrolysis of the esters is of two types:

- Acid catalysed hydrolysis
- Base catalysed hydrolysis

Acid-catalysed hydrolysis of esters:

Acid catalysed hydrolysis of esters is one of the important methods for the preparation of carboxylic acids. Acid-catalysed hydrolysis of esters is ***reversible*** in nature. The overall reaction may be represented as follows:

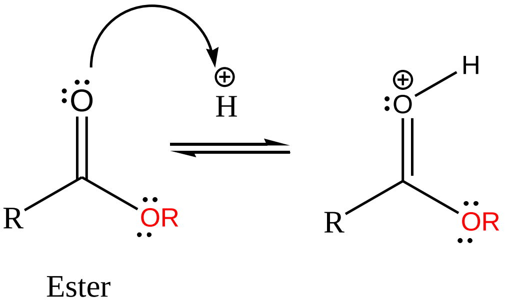


Note: Acid-catalysed hydrolysis of the ester and acid-catalysed ester formation are the exact reverse of each other.

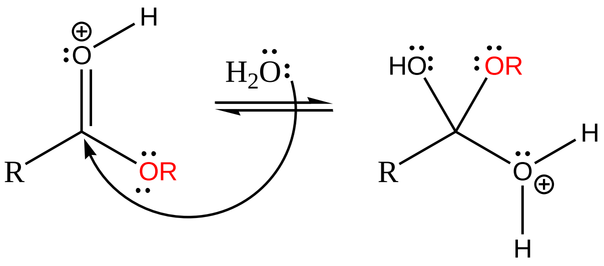
Mechanism:

Mechanism of acid-catalysed hydrolysis of esters involves the following steps:

- Mineral acid protonates the carbonyl oxygen of the ester and makes the carbonyl carbon more susceptible to the nucleophilic attack

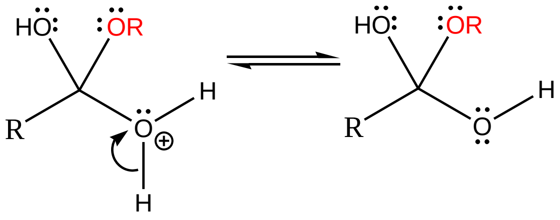


- Nucleophilic addition of water occurs to the protonated ester leading to the formation of **I**



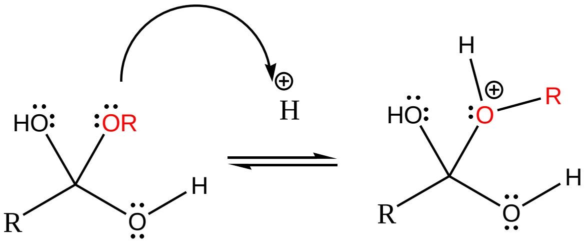
I

- Deprotonation of I to give neutral form of the tetrahedral intermediate

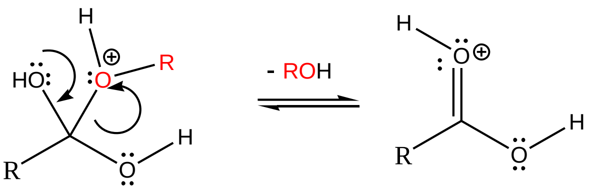


I

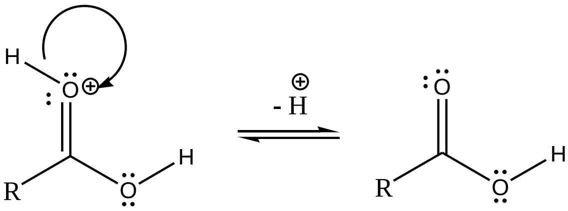
- Protonation of the alkoxy oxygen of the tetrahedral intermediate



- Dissociation of the protonated form of the tetrahedral intermediate gives the alcohol and the protonated form of the carboxylic acid

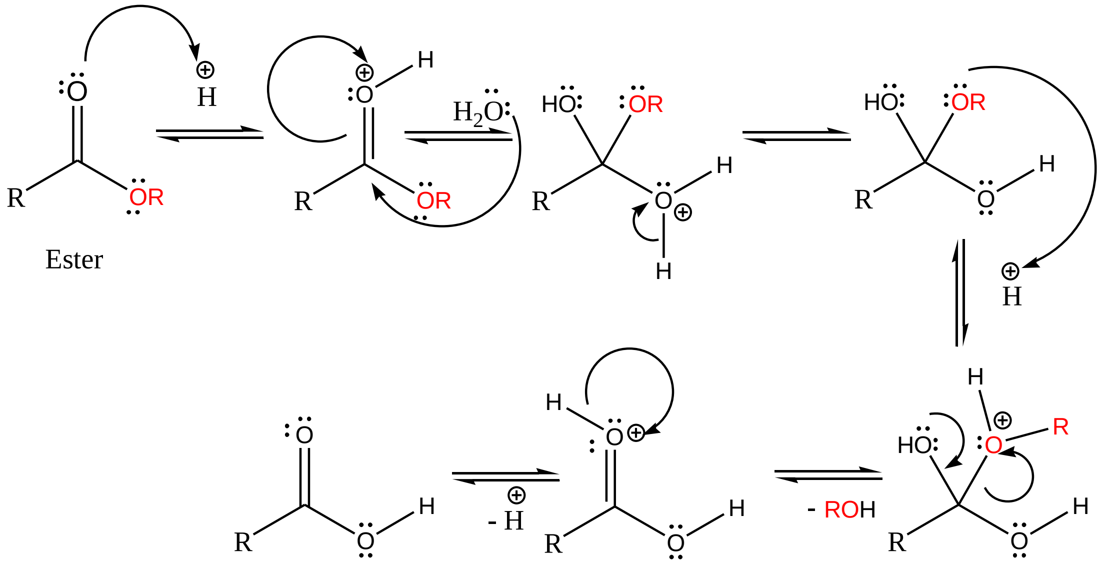


- Deprotonation of the protonated carboxylic acid completes the process



Carboxylic acid

The whole mechanism may also be represented in a sequence as shown below:

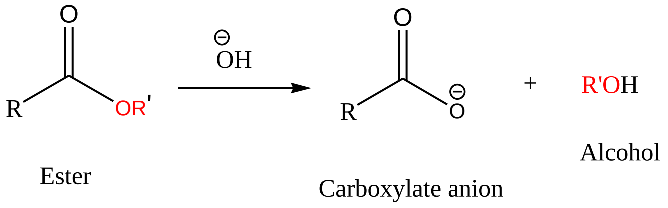


Carboxylic acid

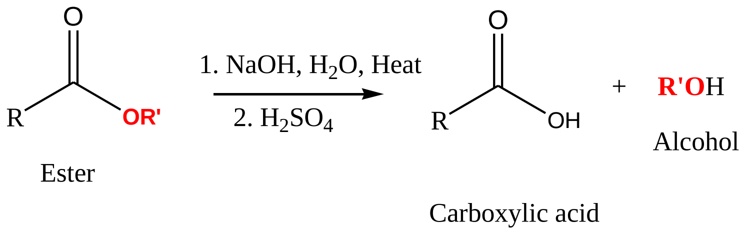
Base-catalysed hydrolysis of esters:

Unlike acid-catalysed hydrolysis of ester, base-catalysed hydrolysis of esters is irreversible in nature. Ester hydrolysis in presence of base is known as ***sponification*** which means ***soap making.***

The overall reaction may be represented as follows:



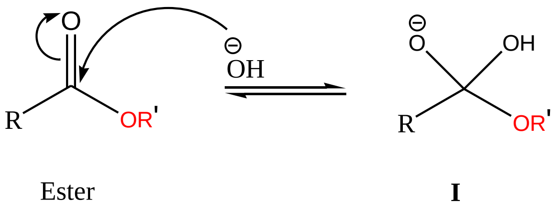
To separate the carboxylic acid, an additional acidification step is carried out and in that case overall reaction may be represented as shown below:



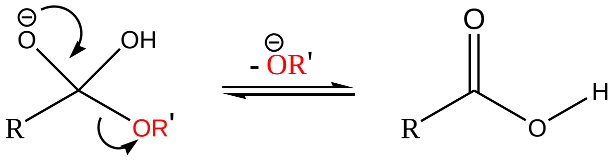
Mechanism:

Mechanism of base-catalysed hydrolysis of esters involves the following steps:

- Nucleophilic addition of the hydroxide ion to the carbonyl group leading to the formation of anionic tetrahedral intermediate I



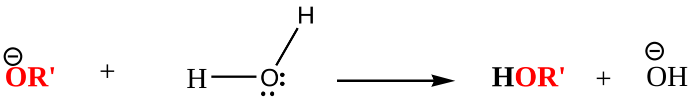
- Dissociation of the anionic tetrahedral intermediate I to carboxylic acid



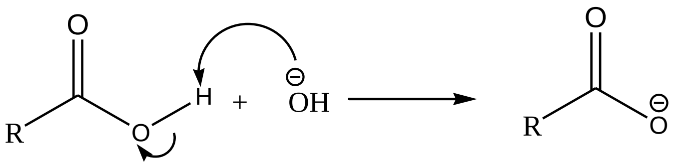
I

Carboxylic acid

- Finally, proton transfers yield an alcohol and a carboxylate anion

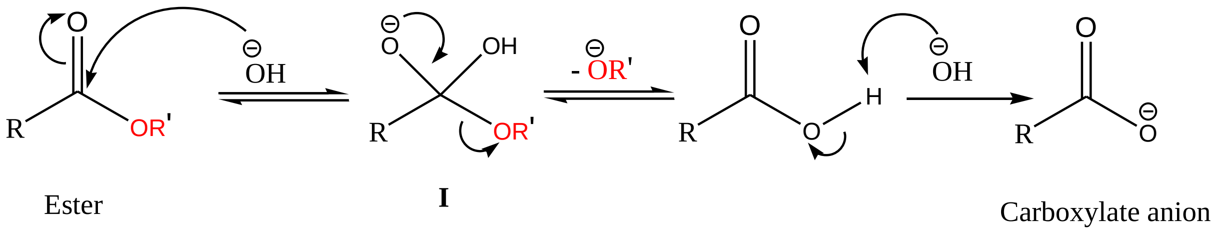


Alcohol



Carboxylate anion

The whole mechanism may also be represented in a sequence as shown below:



Topic 4: Reactions of carboxylic acids: Hell-Volhard-Zelinsky reaction

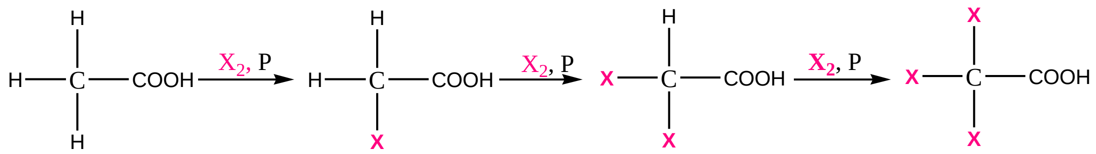
Hell-Volhard-Zelinsky (HVZ) reaction

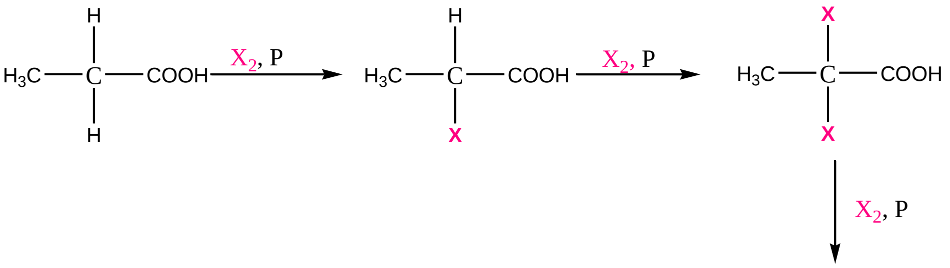
This important reaction of carboxylic acids is named after three chemists:

- ***Carl Magnus von Hell*** (1849–1926) {German chemists}
- ***Jacob Volhard*** (1834–1910) {German chemists}
- ***Nikolay Zelinsky*** (1861–1953). {Russian chemist}

Carboxylic acids do not undergo substitution reactions at α-position under basic conditions because base will remove proton from the -COOH group rather than from α-position. If, however, ***a carboxylic acid containing α-hydrogen is treated with chlorine or bromine in presence of a small amount of phosphorous trihalide then α-hydrogen gets replaced by halogen.*** This halogenation reaction is called Hell–Volhard–Zelinsky reaction or **HVZ reaction** after its discoverers.

In an alternative method, ***elemental phophorous (P)*** is used. ***Elemental phophorous (P) reacts with the halogen to generate the phosphorous trihalide.***





No substitution further

where X = Cl or Br

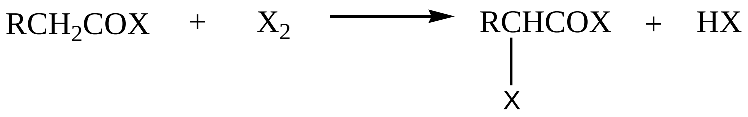
If $\mathbf{PX_3}$ is used in the reaction instead of **P**
then write $\mathbf{PX_3}$ on arrow in place of **P**

Role of phosphorous trihalide in HVZ reaction:

The role of ***phosphorous trihalide*** in this reaction is to ***convert the carboxylic acid into acid halide. In acid halide form, each molecule of the carboxylic acid undergoes α-halogenation***. Go through the following chemical equations to understand the role of phosphorous and phosphorous trihalide (whichever is used in the reaction):

$$P + X_2 \longrightarrow PX_3$$

$$RCH_2COOH + PX_3 \longrightarrow RCH_2COX \quad \text{(Acid halide)}$$



$$RCH_2COX + X_2 \longrightarrow \underset{\displaystyle X}{\underset{|}{RCHCOX}} + HX$$

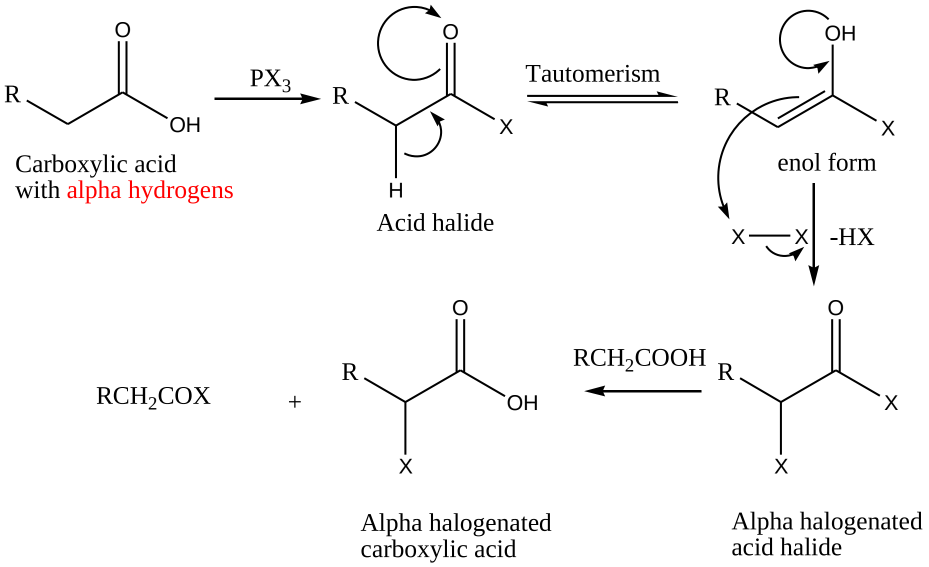
Note: This reaction is not applicable to iodine and fluorine.

Mechanism:

Hell–Volhard–Zelinsky reaction mechanism is quite different from other halogenation reactions as it takes place in ***the absence of any halogen carrier***.

The pathway (i.e. the mechanism) followed by Hell–Volhard–Zelinsky reaction can be summed up in following points:

- PX_3 converts the carboxylic acid into an acid halide
- This acid halide is in equilibrium with its enol form
- Halogenation of the enol forms leads to α-halogenated acid halide
- α-Halogenated acid halide gets converted to the corresponding carboxylic acid



Problems for practice:

Problem 1: Give the mechanism of acid catalysed hydrolysis of esters.

Problem 2: Write a note on Hell-Volhard-Zelinsky reaction.

Problem 3: Discuss alkaline hydrolysis of esters as a method for the synthesis of carboxylic acids.

Reference Books:

- Morrison, R. T. & Boyd, R. N. Organic Chemistry, Dorling Kindersley (India) Pvt. Ltd. (Pearson Education).
- Finar, I. L. Organic Chemistry (Volume 1), Dorling Kindersley (India) Pvt. Ltd. (Pearson Education).
- Carey, F. A. & Giuliano, R. M. Organic Chemistry, McGraw-Hill