

Welcome students, I'm Dr. Chandan

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I'll be taking section B, organic

Chemistry, in paper CHC 103.

Title of the Unit 1 carboxylic acids

and their derivatives. Module name.

Halogenation of carboxylic acid

Hell Volhard Zelinsky reaction.

In this presentation I will be

discussing Hell Volhard Zelinsky

halogenations, its reaction, its mechanism,

Some examples and applications.

In this presentation,

the students will be able to learn.

The definition of Hell

Volhard Zelinsky reaction.

Explanation of the mechanism.

Illustration of some

examples and applications.

Halogenation of carboxylic acid

Hell Volhard Zelinsky reaction.

Aliphatic carboxylic acid having alpha

Hydrogen, in presence of a small amount

of red phosphorus and halogen forms,

Alpha halo carboxylic acid.

This reaction is called Hell Volhard

Zelinsky reaction or HVZ reaction.

In other words,

HVZ reaction is alpha

elimination of carboxylic acid.

This is the general reaction.

Aliphatic carboxylic acid,

$R-CH_2-COOH$  in presence of

phosphorus and halogen  $X_2$ , halogen

X can be bromine or chlorine to

give alpha halo carboxylic acid.

Halogen X is attached to alpha carbon atom.

The HVZ reaction is named

after three chemists, Carl Magnus.

Von Hell and Jacob Volhard.

These are the two German chemists and

the Russian chemist is Nikolai Zelinsky.

For this reaction to take place,  
carboxylic acid should have alpha  
hydrogen atom, only chlorine and bromine  
undergo this reaction, fluorine and  
iodine do not give this reaction and mainly  
alpha substituted products are formed.

Alpha hydrogens means  
hydrogens present on carbon atom  
adjacent to the carbonyl group.

In structure I, carbon adjacent  
to carbonyl is alpha carbon,  
and hydrogens attached to alpha  
carbons are alpha hydrogen atoms.

there are two alpha hydrogens  
attached to alpha carbon in structure I.

In structure II, there is only one  
Alpha hydrogen attached to alpha carbon.

This type of acids will show  
HVZ reaction.

In structure III,  
there are two methyl groups

attached to alpha carbon

and there is no alpha hydrogen for

structure III and for structure IV,

Benzoic acid, an aromatic acid, in this

case also there is no alpha hydrogen,

so this type of carboxylic acids,

do not undergo HVZ halogenation reaction.

This is alpha bromination of carboxylic

Acid. Acid in presence of bromine

and red phosphorus gives alpha bromo

carboxylic acid, bromo is

attached to alpha carbon.

The mechanism of this

reaction involves four steps.

First, formation of  $PBr_3$ ,

that is phosphorus tribromide, by

the action of phosphorus and bromine.

Second, formation of acid bromide

by the action of carboxylic acid and

$PBr_3$ , third, alpha bromination

of acid bromide by bromine and

4<sup>th</sup>, conversion of alpha bromo

acid bromide to product alpha,

Bromo acid.

Step one, red phosphorus with Bromine

forms phosphorus bromide.

Step 2, PBr<sub>3</sub> is a brominating agent,

which replaces carboxylic -OH to Br<sub>2</sub> and

converts carboxylic acid to acid bromide.

Step 3A, bromination of acid bromide

by bromine takes place to give

product, alpha Bromo acid bromide.

In this carbonyl of acid bromide

tautomerizes to enol.

Oxygen takes alpha hydrogen,

To form -OH and carbon.

Carbon double bond is formed.

En means double bond and -OH

means al of the alcohol.

The double bond of the acid

readily attacks bromine to

give alpha bromo acid bromide.

Step four, in presence of unreacted

carboxylic acid exchange of Br

to -OH takes place and thus

alpha bromo acid bromide gets

converted to alpha bromo acid.

There are some example of HVZ

Reactions. Example one, Acetic acid

When treated with phosphorus and chlorine,

gives alpha chloroacetic acid.

There are still 2 alpha Hydrogens.

Further reaction can be carried

out to give dichloroacetic acid

and trichloroacetic acid.

Example two, acetic acid

treated with phosphorus and

bromine gives mono bromoacid.

There is still one more alpha hydrogen.

Further reaction can be carried

out to give dibromoacetic acid.

Application of HVZ reaction.

HVZ reaction can be

used to prepare alpha hydroxyl-acids.

Acetic acid is converted to

alpha bromoacetic acid and

treated with aqueous KOH, potassium hydroxide,

-OH replaces -Br giving

alpha hydroxyl- acetic acid,

which is also called as glycolic acid.

Second, preparation of Alpha- beta

unsaturated acid, where acid is

converted to alpha bromoacid and

treated with alcoholic KOH,

alcoholic KOH means, KOH

dissolved in alcohol like.

ethyl alcohol.

Elimination of HBr takes place giving

double bond at Alpha- beta position,

and alpha-beta unsaturated acid is formed.

3<sup>rd</sup>, preparation of alpha aminoacid.

here, acid is converted to alpha bromo

acid and treated with ammonia.  $-NH_2$

replaces -Br to give alpha aminoacid.

Example, acetic acid is converted to bromo

acetic acid and treated with ammonia

to give alpha amino acetic acid.

It is also called glycine.

Fourth, preparation of dicarboxylic acid.

Acetic acid is converted to alpha bromo

acetic acid and then treated with KCN,

potassium cyanide. Here cyano replaces

Br and gives alpha cyano-acetic acid.

Hydrolysis of cyano gives COOH and

That's how dicarboxylic acid is formed.

In this case it is malonic acid.

To summarize.

Hell Volhard Zelinsky is alpha

bromination of carboxylic acid.

Only bromine and chlorine

undergo this reaction.

And Fluorine and Iodine do

not give this reaction.

Various important intermediates

like alpha amino acids,

alpha hydroxyacids,

alpha, Cyano-acids,

diacids like malonic acid, etc

can be prepared using this

Hell Volhard Zelinsky reaction.

Students for your further knowledge,

you can refer these books. Thank you.