

Quadrant II – Transcript and Related Materials

Programme: Bachelor of Science (Second year)

Subject: Chemistry

Paper Code: CHC-103

Paper Title: Physical chemistry and Organic chemistry

Unit: 1

Module Name: Hell Volhard Zelinsky reaction

Module No:03

Name of the Presenter: Dr. Chandan P. Amonkar

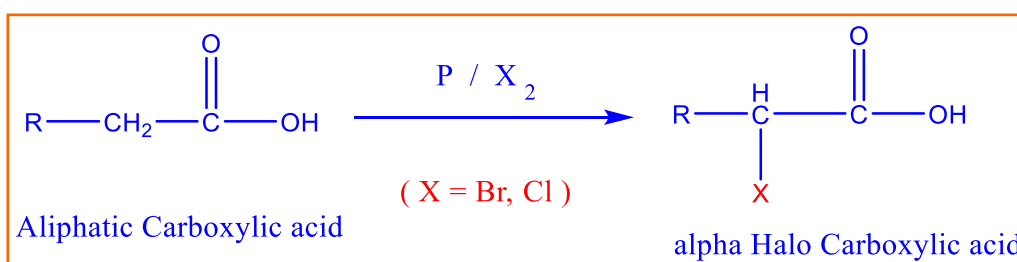
Notes

Halogenation of Carboxylic acid

Hell-Volhard-Zelinsky Reaction: (HVZ reaction)

Carboxylic acid in presence of Red Phosphorus and halogen forms alpha halo-carboxylic acid. This reaction is known as Hell-Volhard-Zelinsky Reaction (HVZ reaction). H.V. Z. reaction is α - halogenation of carboxylic acid

General Reaction of H.V. Z. Halogenation



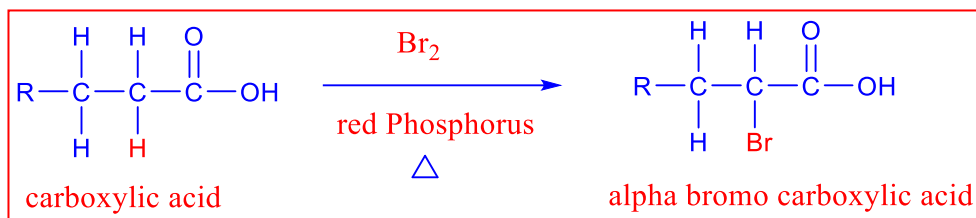
The H.V.Z. reaction is named after three chemists: Carl Magnus von Hell - (German)

Jacob Volhard - (German) & Nikolay Zelinsky - (Russian)

Carboxylic acid should have alpha hydrogen atom. Only chlorine (Cl_2) and bromine (Br_2) undergo this reaction. Fluorine (F) and Iodine (I_2) do not give this reaction. Mainly alpha substituted products are formed.

Alpha Hydrogens: Hydrogens present on carbon atom adjacent to the carbonyl group (C=O). The carboxylic acids without alpha hydrogen do not undergo H.V.Z. halogenation reaction

α – Bromination of carboxylic acid

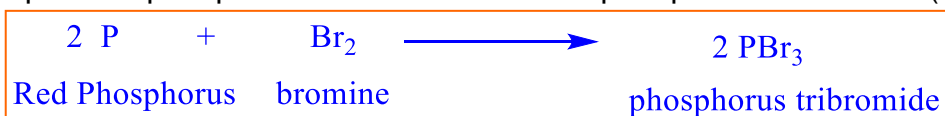


Mechanism:

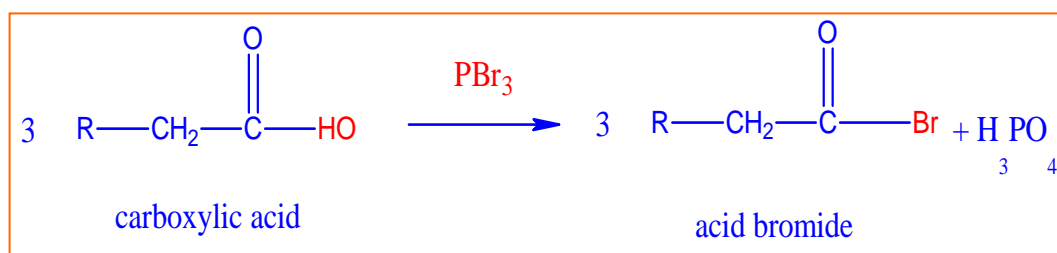
The H.V. Z. mechanism involves 4 steps:

- 1) Formation of PBr_3 (phosphorus tribromide) by the action of P and Br_2
- 2) Formation of acid bromide by reaction of carboxylic acid and PBr_3
- 3) Alpha bromination of acid bromide by Br_2
- 4) Conversion of α - bromo acid bromide to product α - bromo acid.

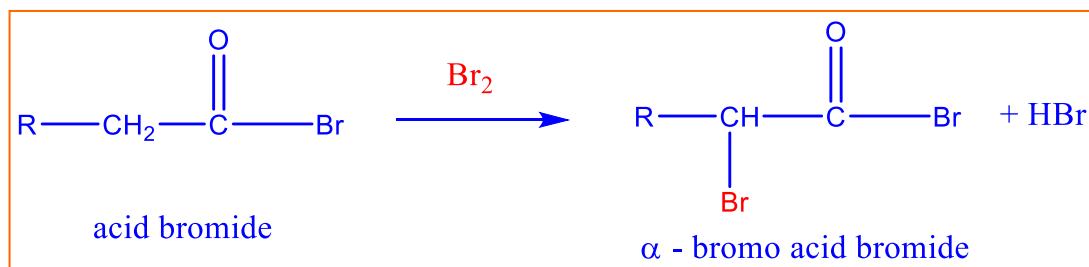
Step1: Red phosphorus with bromine forms phosphorus tribromide (PBr_3)



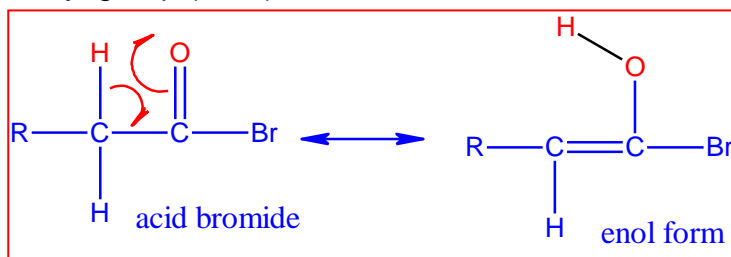
Step 2: PBr_3 is a brominating agent. It replaces carboxylic $-\text{OH}$ group to $-\text{Br}$ (Converts carboxylic acid to acid bromide)



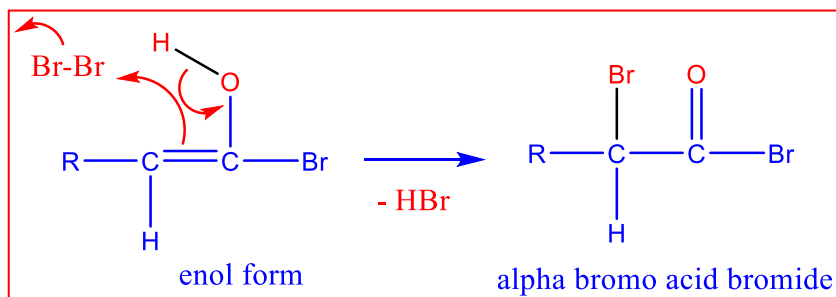
Step 3: Alpha bromination of acid bromide by Br_2 to give product α - bromo acid bromide



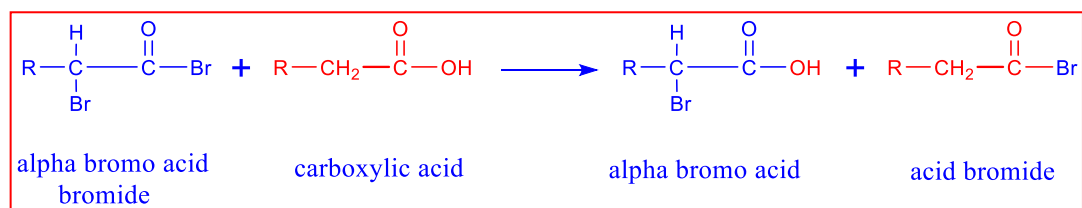
Carbonyl group (C=O) of acid bromide tautomerizes to *enol*



Enol readily attacks Bromine to give α -bromo acid bromide

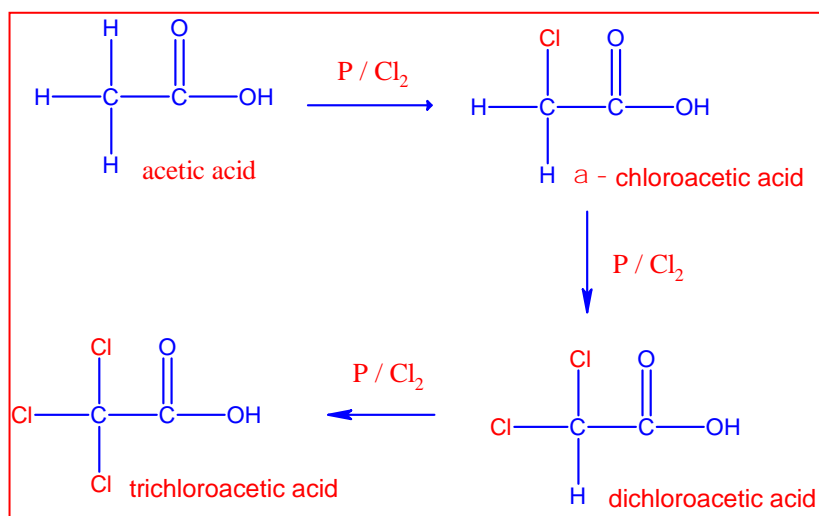


Step 4: In presence of unreacted carboxylic acid, exchange of -Br to -OH takes place
Thus, α - bromo acid bromide gets converted to α - bromo acid

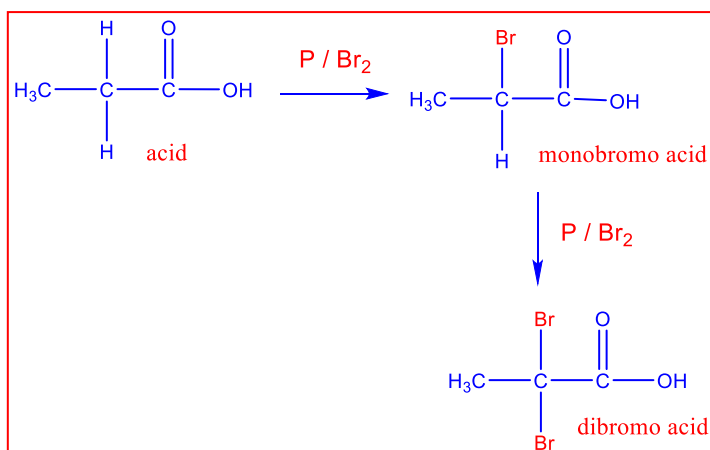


Some examples of H.V.Z. reactions:

Example 1:

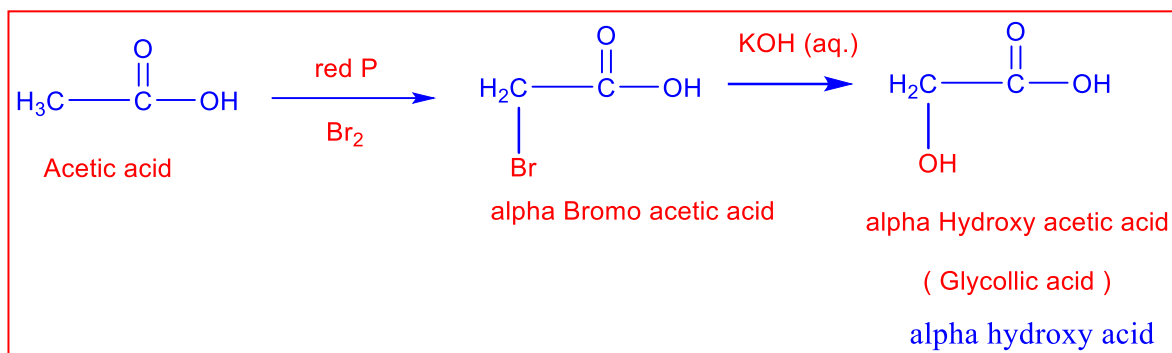


Example 2:

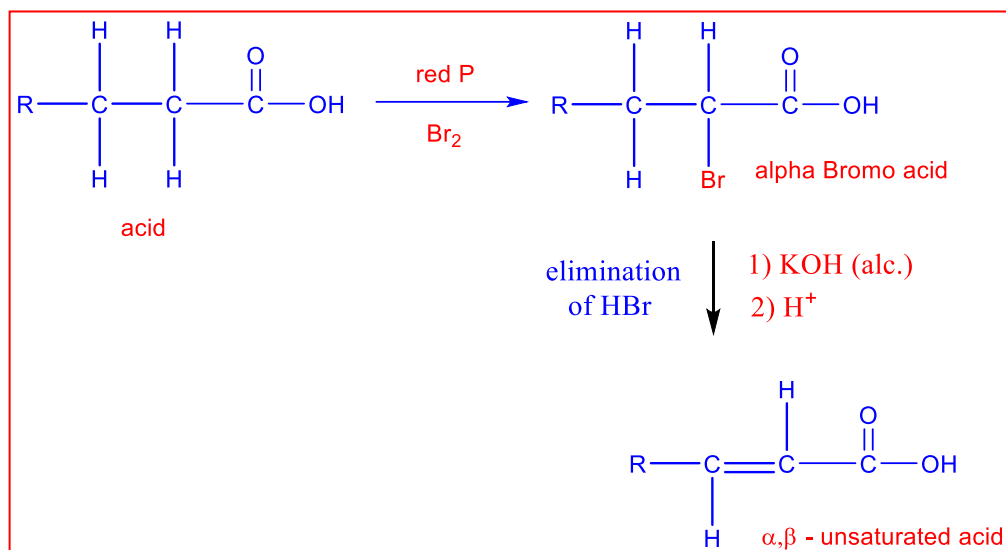


Applications of H.V. Z. Reaction:

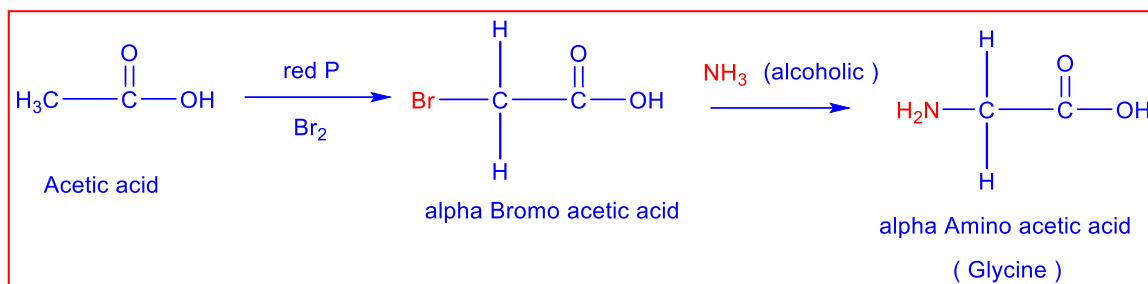
- 1) Preparation of alpha hydroxy acids: Acid is converted to alpha bromo acid by HVZ reaction and subjected to aqueous KOH to give alpha hydroxy acid.



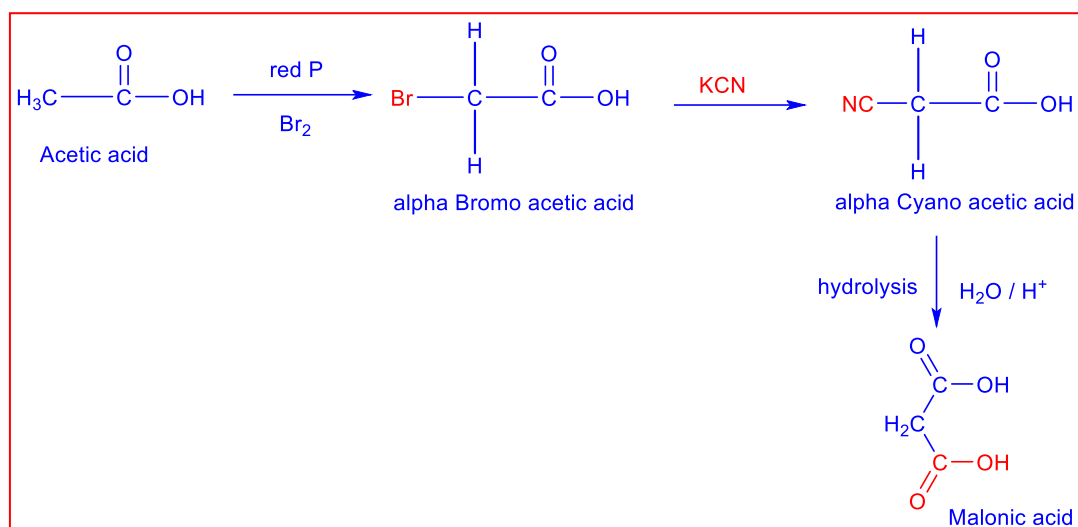
- 2) Preparation of α, β - unsaturated acids: Acid is converted to alpha bromo acid and subjected to alcoholic KOH to give alpha, beta –unsaturated acid by elimination of HBr.



- 3) Preparation of α - amino acids: Alpha bromo acid is formed from acid and subjected to ammonia to yield alpha amino acid.



- 4) Preparation of di-carboxylic acid: Acid is converted to alpha bromo acid by HVZ reaction and further subjected to KCN to give alpha cyano acid, which on hydrolysis gave a dicarboxylic acid.



To summarize, Hell Volhard Zelinsky reaction is alpha halogenation of carboxylic acid. Only Br_2 and Cl_2 undergo this reaction in presence of red phosphorus. Halogens like F & I_2 do not give this reaction. Various important intermediates like alpha amino acids, alpha hydroxy acid, alpha cyano acids, Malonic acid, etc. are prepared using this H.V. Z. reaction.