▶ Video explanation (YouTube Short)

HVZ Reaction and Ring Substitution in Carboxylic Acids

Two places where a carboxylic acid can be substituted: the **α-carbon** next to –COOH (Hell-Volhard-Zelinsky reaction) and, in aromatic acids, the **benzene ring** (NCERT 8.9.4).

1. Hell-Volhard-Zelinsky (HVZ) reaction

$R–CH_2–COOH \xrightarrow{\text{(i) } X_2 \text{ / red P, (ii) } H_2O} R–CHX–COOH$ (X = Cl, Br)

Point	Detail
Reagents	Cl_2 or Br_2 with a small amount of red phosphorus, then water
What changes	one α-hydrogen is replaced by the halogen
Condition	the acid must have at least one α-hydrogen
Example	$CH_3COOH \rightarrow ClCH_2COOH$ (chloroacetic acid)
Use	α-halo acids are starting materials for many other compounds

2. Ring substitution: –COOH is deactivating and meta-directing

The carbonyl group pulls the ring's π electrons towards itself: a ring C=C pair moves into the ring–C bond while the C=O π pair moves onto oxygen. The resonance structures carry a positive charge at the **ortho** and **para** carbons, so the ring is less reactive (deactivated) and an incoming electrophile goes to the **meta** carbon, which is least electron-poor.

Reaction	Reagent	Product from benzoic acid
Nitration	conc. HNO_3 + conc. H_2SO_4	m-nitrobenzoic acid
Bromination	Br_2 / $FeBr_3$	m-bromobenzoic acid

3. No Friedel-Crafts reaction

Aromatic carboxylic acids do not undergo Friedel-Crafts alkylation or acylation: the ring is deactivated, and the catalyst $AlCl_3$ (a Lewis acid) bonds to the carboxyl group.

Solved example

Q. Will 2,2-dimethylpropanoic acid, $(CH_3)_3C–COOH$, undergo the HVZ reaction?
A. No. Its α-carbon carries three CH_3 groups and no hydrogen, and HVZ needs at least one α-hydrogen.

Key takeaways

- HVZ: X_2 / red P, then H_2O → α-halo acid; needs an α-H.
- $CH_3COOH \rightarrow ClCH_2COOH$.
- On a benzene ring, –COOH is deactivating and meta-directing.
- Benzoic acid → m-nitrobenzoic acid (nitration), m-bromobenzoic acid (bromination).

- No Friedel-Crafts reaction for aromatic acids.

Practice questions

1. (MCQ) The HVZ reaction uses: (a) Br_2 / $FeBr_3$ (b) Br_2 / red P, then H_2O (c) NaOH / CaO (d) $LiAlH_4$
2. (MCQ) Nitration of benzoic acid gives mainly: (a) o-nitrobenzoic acid (b) p-nitrobenzoic acid (c) m-nitrobenzoic acid (d) nitrobenzene
3. (MCQ) Which acid does not undergo the HVZ reaction? (a) CH_3COOH (b) CH_3CH_2COOH (c) $(CH_3)_3CCOOH$ (d) $(CH_3)_2CHCOOH$
4. (Very short) Name the product of CH_3COOH with Cl_2 / red P, followed by water.
5. (Very short) Is –COOH activating or deactivating towards electrophilic substitution?
6. (Short) Why does an electrophile attack the meta position of benzoic acid?
7. (Short) Give two reasons why benzoic acid does not undergo Friedel-Crafts reaction.
8. (Application) Write the product when propanoic acid is treated with Br_2 / red P and then water.

Answer key

1. (b) Br_2 / red P, then H_2O.
2. (c) m-nitrobenzoic acid.
3. (c) $(CH_3)_3CCOOH$: no α-hydrogen.
4. $ClCH_2COOH$, chloroacetic acid.
5. Deactivating (and meta-directing).
6. Resonance with the C=O group leaves positive charge at the ortho and para carbons; the meta carbon is least electron-poor, so the electrophile goes there.
7. The ring is deactivated by –COOH, and the catalyst $AlCl_3$ bonds to the carboxyl group.
8. $CH_3CHBrCOOH$, 2-bromopropanoic acid.

▶ Watch the video explanation