LOGIC BLOOM · CHEMISTRY · CLASS 12

Aldehydes, Ketones and Carboxylic Acids

Organic Chemistry · **NEET, JEE Main and JEE Advanced**

One polar bond explains this entire chapter. The oxygen has already pulled the pi cloud away, so the carbon is hungry for electrons and nucleophiles queue up to attack it. Everything else, every reagent and every named reaction, is a consequence of that single fact.

11 Sections | 10 Diagrams | Advanced Tier | Trap Alerts | Fact Sheet

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Simplest way to understand the NCERT.

Contents

0 How to Read This Set

This chapter is built in two tiers. Sections 1 to 7 are the full syllabus for **NEET and JEE Main**. Sections 8 to 11 are the **JEE Advanced** layer, where you are asked to explain the mechanism and predict the stereochemistry rather than just name a product.

THE WHOLE CHAPTER IN ONE LINE

The carbonyl carbon is electron poor, so nucleophiles attack it.

Alkenes react with electrophiles. Carbonyls do the exact opposite, because the oxygen has already pulled the pi cloud away from the carbon.

THINK IT THROUGH

HOW TO USE THE TWO TIERS

- If you are sitting **NEET or JEE Main**, sections 1 to 7 plus the fact sheet are complete. Nothing in the Advanced tier will be asked of you.
- If you are sitting **JEE Advanced**, read all eleven. The last four are where the marks separate candidates, because they cannot be answered from memory.
- Read each section, then study the drawing beside it. The drawings carry information the prose deliberately does not repeat.

TRAP ALERT

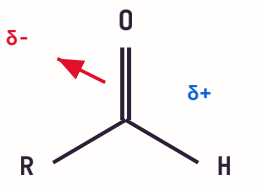
THE ONE HABIT THAT FIXES THIS CHAPTER

- Before writing any product, ask two questions in this order.
- **One:** is this an aldehyde or a ketone? That fixes the **reactivity**.
- **Two:** does it have an **alpha hydrogen**? That decides whether it can give an aldol at all, or must give Cannizzaro instead.
- Almost every wrong answer in this chapter comes from skipping the second question.

1 The Carbonyl Group

The carbon and oxygen are joined by a double bond, exactly as two carbons are in an alkene. But oxygen is far more electronegative, so it drags the pi cloud towards itself. That single difference reverses the chemistry.

THE CARBONYL GROUP: ONE POLAR BOND EXPLAINS THE WHOLE CHAPTER



the C=O bond

O is far more electronegative, so it pulls the pi cloud across

THE CARBON IS ELECTRON POOR

so a NUCLEOPHILE attacks it

Nu- adds across the C=O

THE OXYGEN IS ELECTRON RICH

so an ELECTROPHILE, often H+, attaches there first

WHY IT MATTERS

The carbon is sp2, so the **group is TRIGONAL PLANAR** with 120° angles.

Alkenes react with **ELECTROPHILES.**

Carbonyls react with **NUCLEOPHILES.**

Same bond, opposite behaviour.

Same double bond as an alkene, opposite behaviour, purely because of polarity.

The carbon is **sp^2** hybridised, so the group is trigonal planar with bond angles near 120°. That flatness matters later, because it is why addition products come out racemic.

THINK IT THROUGH

PHYSICAL PROPERTIES WORTH REMEMBERING

- Carbonyl compounds have **no O-H**, so they cannot hydrogen bond to each other. Their boiling points sit **between** alkanes and alcohols of similar mass.
- They *can* accept hydrogen bonds from water, so the lower members dissolve well.
- Carboxylic acids form **dimers** through two hydrogen bonds, so they boil higher than alcohols of comparable mass.

2 Preparation

The routine routes

STARTING MATERIAL	REAGENT	PRODUCT
1° alcohol	PCC, or Cu at 573 K	aldehyde
2° alcohol	PCC or $K_2Cr_2O_7$	ketone
alkyne	H_2O / H_2SO_4, $HgSO_4$	ethyne gives ethanal, others give ketones
alkene	O_3, then Zn / H_2O	aldehyde and ketone (ozonolysis)
acyl chloride	H_2 / Pd-$BaSO_4$	aldehyde (Rosenmund)
nitrile	DIBAL-H, or $SnCl_2$/HCl	aldehyde
ester	DIBAL-H	aldehyde

The four named preparations

Each of these is defined by what stops the reaction going too far.

TRAP ALERT

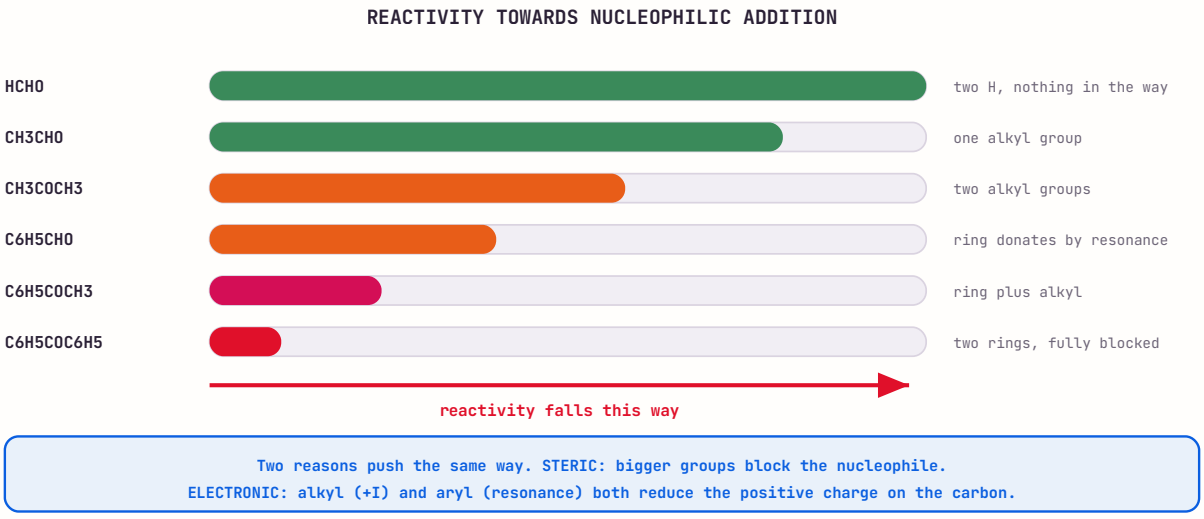
WHY THE CATALYST IS POISONED ON PURPOSE

In **Rosenmund reduction** the palladium is deliberately poisoned with $BaSO_4$ and sulfur.

Without the poison the reaction would run straight past the aldehyde to the alcohol. The same idea appears in Lindlar's catalyst. A poisoned catalyst is not a weaker catalyst, it is a catalyst that has been told where to stop.

3 Nucleophilic Addition

The nucleophile attacks the carbon. The pi electrons move onto the oxygen, which becomes an alkoxide, and a proton then picks it up. The carbon changes from planar sp^2 to tetrahedral sp^3.



Aldehydes always beat ketones, and aliphatic always beats aromatic.

REAGENT	PRODUCT	NOTE
HCN	cyanohydrin	adds one carbon; hydrolysis then gives a hydroxy acid
$NaHSO_3$	bisulfite addition compound	crystalline, so it is used to **purify** carbonyls
R-MgX, then H_2O	alcohol	HCHO gives 1°, other aldehydes 2°, ketones 3°
alcohol / dry HCl	hemiacetal, then acetal	acetals are used to protect a carbonyl group
NH_2-OH	oxime	addition, then elimination of water
NH_2-NH_2	hydrazone	2,4-DNP gives the orange test precipitate

THINK IT THROUGH

THE BISULFITE TRICK

The $NaHSO_3$ adduct is a solid you can filter off, and dilute acid or alkali regenerates the original carbonyl. So it is a purification tool, not just a reaction. It works for aldehydes and for **methyl ketones**, but bulkier ketones are too hindered.

▶ PLAY

REACTIONS BLURRING TOGETHER?

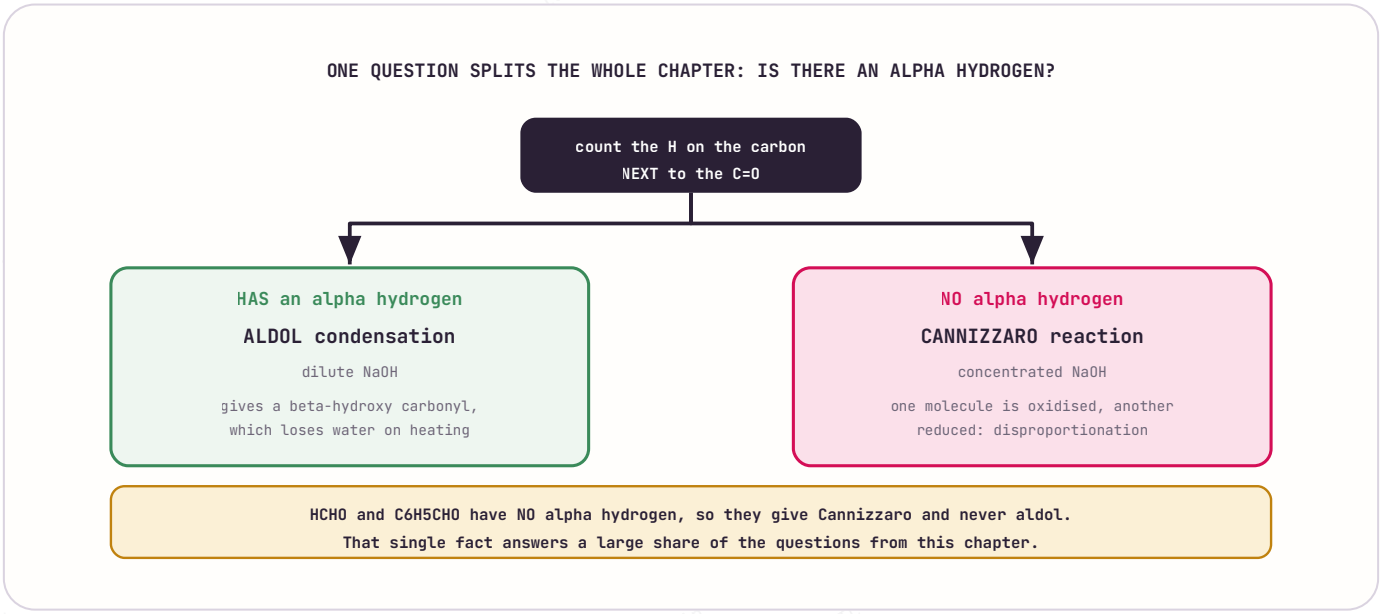
Sort the carbonyls by reactivity yourself.

Drag groups on and off the carbonyl and watch the reactivity bar move. The order stops being a list to memorise. **logicbloom.co.in/download** · Free to start.

SCAN

4 The Alpha Hydrogen Fork

The hydrogen on the carbon next to the carbonyl is acidic, because the anion left behind is stabilised by the C=O. Whether a compound has one decides which reaction it can give at all.



Ask this one question before writing anything else.

Aldol condensation

```
2 CH3CHO  +  dil. NaOH  →  CH3-CH(OH)-CH2-CHO
```

The product is a **beta-hydroxy aldehyde**. On heating it loses water to give an alpha, beta-unsaturated carbonyl. A **cross aldol** between two different partners that both have alpha hydrogens gives four products, which is why it is rarely useful.

Cannizzaro reaction

```
2 HCHO  +  conc. NaOH  →  CH3OH  +  HCOONa
```

One molecule is **oxidised** to the acid salt, the other **reduced** to the alcohol. In a **crossed** Cannizzaro with HCHO present, formaldehyde is always the one oxidised, because it is the better hydride donor.

5 Oxidation and Reduction

REAGENT	DOES WHAT	APPLIES TO
Tollens' / Fehling's	gentle oxidation to the acid	aldehydes only
$KMnO_4$ or $K_2Cr_2O_7$	oxidation to the acid	aldehydes; ketones need harsh conditions and cleave
$NaBH_4$ or $LiAlH_4$	reduction to the alcohol	both aldehydes and ketones
Zn-Hg / conc. HCl	C=O all the way to CH_2	**Clemmensen**, acidic conditions
NH_2NH_2 / KOH, glycol	C=O all the way to CH_2	**Wolff-Kishner**, basic conditions

TRAP ALERT

CLEMMENSEN OR WOLFF-KISHNER: PICK BY WHAT ELSE IS IN THE MOLECULE

Both convert C=O into CH_2, so the choice is never about the carbonyl. Use **Wolff-Kishner** if the molecule has an acid-sensitive group, and **Clemmensen** if it has a base-sensitive one. A question that mentions another functional group is telling you which to pick.

6 Telling Them Apart

Run the tests in this order. Each one narrows the field: carbonyl or not, then aldehyde or ketone, then aliphatic or aromatic.

WHICH TEST TELLS WHAT APART

TEST	WHAT YOU SEE	WHAT IT PROVES
2,4-DNP (Brady's)	orange or yellow ppt	any carbonyl: aldehyde OR ketone
Tollens'	silver mirror	aldehyde only, aliphatic and aromatic
Fehling's / Benedict's	red Cu2O	ALIPHATIC aldehyde only
Iodoform, I2 + NaOH	yellow CHI3 crystals	CH3CO- group, or CH3CH(OH)-
NaHCO3	brisk effervescence	carboxylic acid, NOT phenol

The pair examiners use most: Tollens' works for BOTH aliphatic and aromatic aldehydes, but Fehling's refuses benzaldehyde. That is how you separate the two aldehydes.

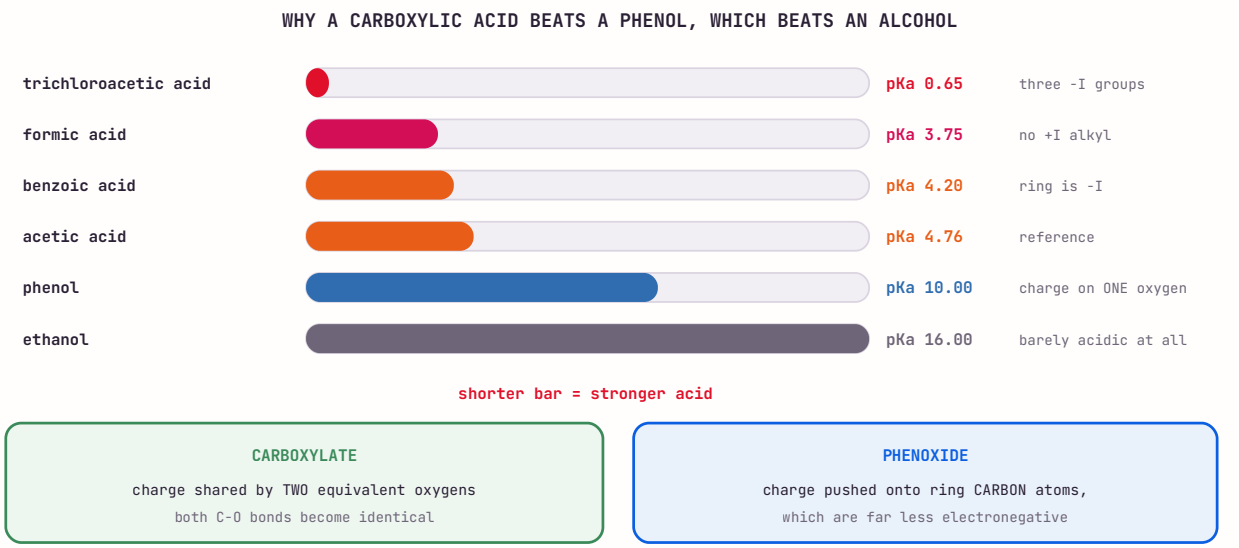
Five tests, and what each one actually proves.

THINK IT THROUGH

THE IODOFORM TEST IS NOT ABOUT ALDEHYDES

It is positive for a CH_3CO- group, or a $CH_3CH(OH)$- group which oxidises to it. So ethanal gives it, propanone gives it and ethanol gives it, but propanal and methanol do not. Read the structure, not the family.

7 Carboxylic Acids



The whole order comes from how well the negative charge is spread once the proton leaves.

THINK IT THROUGH

THE ARGUMENT IN THREE STEPS

- An alkoxide has its charge on **one** oxygen with nothing to share it, so an alcohol is barely acidic.
- A phenoxide spreads the charge into the ring, but onto **carbon** atoms, which hold it poorly.
- A carboxylate spreads it over **two equivalent oxygen atoms**, and both C-O bonds become identical in length. That is the best stabilisation of the three.

What changes the strength

CHANGE	EFFECT	BECAUSE
add -I groups (Cl, NO_2, F)	stronger	the anion is stabilised
add more of them	stronger still	trichloroacetic beats dichloro beats chloro
move the -I group away	weaker	induction fades after about three carbons
add +I alkyl groups	weaker	acetic acid is weaker than formic
-NO_2 on a benzoic ring	stronger	-M and -I both pull
-OCH_3 at the para position	weaker	+M pushes density in

Reactions of the -COOH group

REAGENT	PRODUCT	NOTE
$NaHCO_3$	salt + CO_2 + H_2O	the test that separates acids from phenols
alcohol / conc. H_2SO_4	ester	esterification, and it is reversible
PCl_5, PCl_3 or $SOCl_2$	acyl chloride	$SOCl_2$ is preferred, since the by-products are gases
NH_3, then heat	amide	goes through the ammonium salt
$LiAlH_4$	1° alcohol	$NaBH_4$ is too mild to touch a -COOH
Cl_2 / red P	alpha-chloro acid	**Hell-Volhard-Zelinsky**, needs an alpha hydrogen
soda lime, heat	alkane	decarboxylation, loses CO_2

TRAP ALERT

THREE THINGS STUDENTS LOSE MARKS ON

- **$NaBH_4$ does not reduce a carboxylic acid**. Only $LiAlH_4$ or diborane will.
- **HVZ needs an alpha hydrogen**, so benzoic acid and formic acid cannot give it.
- Formic acid has an aldehyde group hidden inside it, so it is the one carboxylic acid that **reduces Tollens and Fehling reagents**.

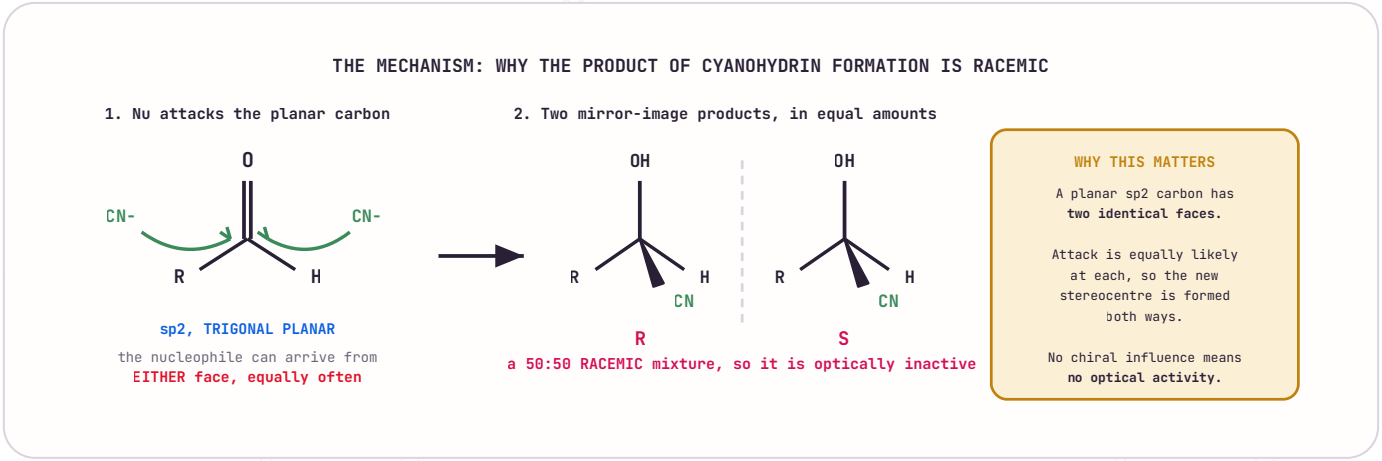
TIER 2

The JEE Advanced layer

Everything so far is complete for NEET and JEE Main. Advanced asks you to explain why, and to predict stereochemistry. That is what the next four sections add.

8 Mechanism and Stereochemistry

Advanced questions rarely ask for the product alone. They ask which face was attacked, what the intermediate was, and whether the product turns out optically active.



A planar carbonyl has two identical faces, so a new stereocentre forms both ways in equal amounts.

THINK IT THROUGH

THREE MECHANISMS WORTH WRITING OUT ONCE

- **Aldol:** base removes the alpha hydrogen to give an **enolate**. That enolate is the nucleophile, and it attacks a second carbonyl.
- **Cannizzaro:** hydroxide adds to the carbonyl, then a **hydride** shifts from that intermediate to a second molecule. It is an internal redox, which is exactly why it needs no alpha hydrogen.
- **Acetal formation:** needs **dry HCl**. The acid protonates the oxygen first, which makes the carbon far more electrophilic. Water present would reverse the whole thing.

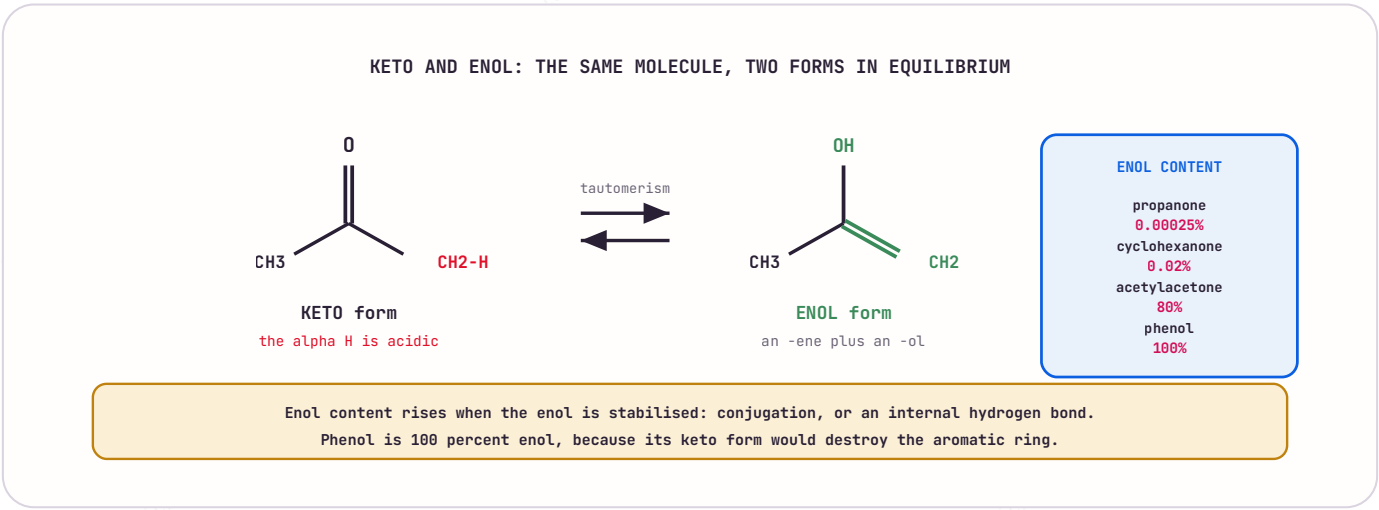
TRAP ALERT

WHY SEMICARBAZIDE REACTS AT ONLY ONE NITROGEN

Semicarbazide has **two** NH_2 groups, yet only one forms the semicarbazone. The other nitrogen has its lone pair delocalised into the neighbouring C=O, so it is no longer available to act as a nucleophile. Same molecule, two nitrogens, only one of them free.

9 Keto and Enol Forms

An alpha hydrogen can move to the carbonyl oxygen. The two forms are **tautomers**: real, separate structures in equilibrium, not resonance forms of one structure.



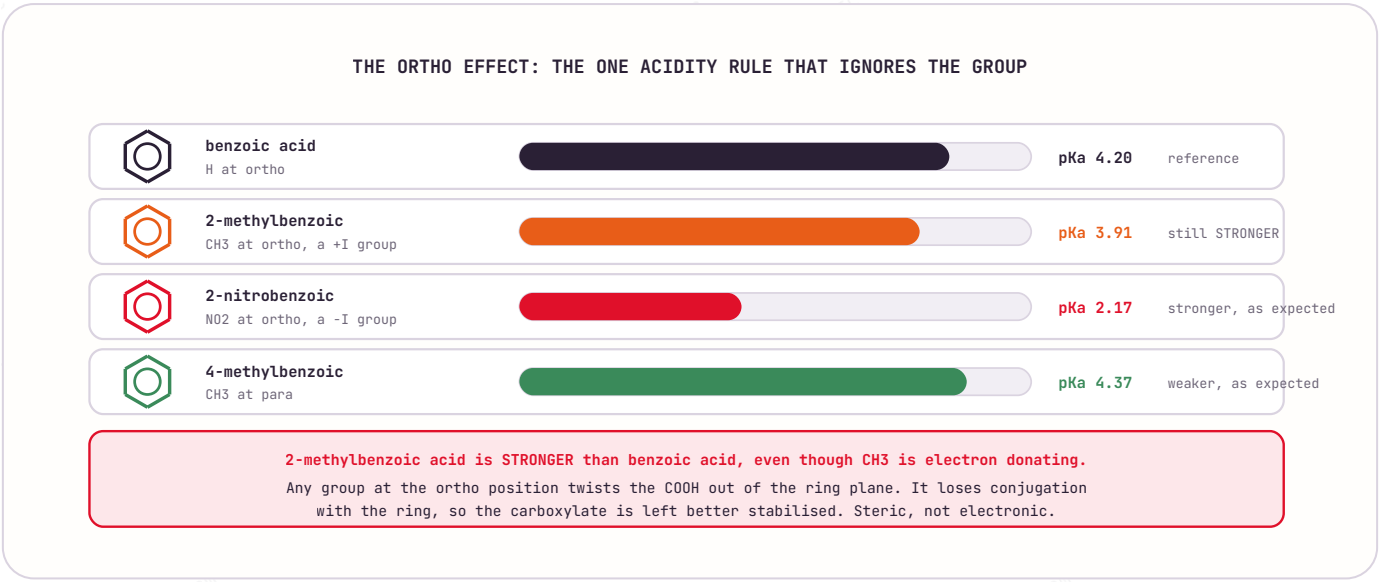
Enol content is tiny for a simple ketone, but rises sharply when the enol is stabilised.

THINK IT THROUGH

RESONANCE AND TAUTOMERISM ARE NOT THE SAME THING

- Resonance structures differ only in where the **electrons** are drawn. They are not real, separate species.
- Tautomers differ in where an **atom** sits, here a hydrogen. Both are real and can in principle be isolated.
- Acetylacetone is about **80 percent enol**, because its enol is conjugated *and* held by an internal hydrogen bond. Phenol is **100 percent enol**, since its keto form would break aromaticity.

10 The Ortho Effect



The proof is the contrast between the two methyl compounds: ortho strengthens, para weakens.

TRAP ALERT

THE RULE THAT IGNORES WHETHER THE GROUP PUSHES OR PULLS

Every ortho-substituted benzoic acid is stronger than benzoic acid itself, whether the group is electron donating or withdrawing. A group at the ortho position twists the -COOH out of the ring plane, so it can no longer conjugate with the ring, and the carboxylate ends up better stabilised. The cause is **steric**, not electronic, which is precisely why the usual +I and -I reasoning fails here.

11 Acid Derivatives

One order governs every interconversion. You can move down it freely, never up.

REACTION	WHAT IT DOES	CONDITION
Baeyer-Villiger	inserts an O **next to** the carbonyl, giving an ester	a peroxy acid, such as mCPBA
Perkin	aromatic aldehyde to an unsaturated acid	anhydride and its sodium salt
Benzoin condensation	joins two benzaldehydes	aqueous ethanolic KCN
Hunsdiecker	silver salt of an acid to an alkyl halide	Br_2; the chain shortens by one carbon
Kolbe electrolysis	carboxylate salt to an alkane	electrolysis; the chain doubles
HVZ	alpha-halogenation of an acid	Cl_2 / red P, needs an alpha hydrogen

THINK IT THROUGH

BAEYER-VILLIGER: WHICH GROUP MIGRATES

The oxygen inserts on the side of the group that migrates best, and the order is **tertiary alkyl > cyclohexyl > secondary > phenyl > primary > methyl**. So an unsymmetrical ketone gives one ester in large excess rather than a mixture. Advanced questions turn on picking the right side.

▶ PLAY

MECHANISMS STILL FEEL LIKE MEMORISING?

Push the arrows yourself and watch the intermediate form.

Run the aldol and Cannizzaro step by step, then flip a carbonyl over and see why the product comes out racemic. **logicbloom.co.in/download** · Free to start.

SCAN

★ Aldehydes, Ketones and Carboxylic Acids · Fact Sheet

Every rule for revision day. Print this page alone.

THE CARBONYL

C is δ+, O is δ−

sp^2, trigonal planar, 120°
Nucleophiles attack the carbon.

REACTIVITY ORDER

HCHO > CH3CHO > CH3COCH3

> C6H5CHO > C6H5COCH3
Steric and electronic agree.

NAMED PREPS

Rosenmund: acyl chloride

Stephen: nitrile
Etard and Gattermann-Koch: ring.

THE ALPHA FORK

Has alpha-H: ALDOL, dil. NaOH

No alpha-H: CANNIZZARO, conc. NaOH
HCHO and PhCHO give Cannizzaro.

C=O TO CH2

Clemmensen: Zn-Hg / HCl, acidic

Wolff-Kishner: NH2NH2 / KOH, basic
Choose by the other group.

THE TESTS

2,4-DNP: any carbonyl

Tollens: any aldehyde
Fehling: ALIPHATIC aldehyde only.

IODOFORM

CH3CO- or CH3CH(OH)-

Ethanal, propanone, ethanol yes
Propanal and methanol no.

ACIDITY ORDER

Cl3CCOOH > HCOOH > C6H5COOH

> CH3COOH > phenol > ethanol
Carboxylate: charge on TWO O.

COOH REACTIONS

NaBH4 will NOT reduce it

HVZ needs an alpha-H
HCOOH reduces Tollens.

STEREOCHEMISTRY

Planar sp^2 has two faces

Cyanohydrin comes out RACEMIC
so it is optically inactive.

ENOL CONTENT

Propanone 0.00025%

Acetylacetone 80%
Phenol 100%, to keep aromaticity.

ORTHO EFFECT

ALL ortho-substituted benzoic

acids beat benzoic acid.
Steric, not electronic.

Logic Bloom

Simplest way to understand the NCERT.

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★ CARBONYL REACTIONS STILL RUNNING TOGETHER?

Play it. Then practice it.

Open Aldehydes and Ketones in the Logic Bloom app. Push the arrows through an aldol, watch a cyanohydrin form on both faces, then drill the tests until you recognise them on sight. Free to start.

SCAN → PLAY · READ · PRACTICE