JEE MAIN · PAPER 1 · CHEMISTRY

14 Basic Principles of Organic Chemistry

Formula & concept sheet

The toolkit for all of organic chemistry: how compounds are named, every kind of isomerism and how to count isomers, electronic effects (inductive, resonance, hyperconjugation), reactive intermediates, aromaticity, the orders of acidity and basicity, and the types of organic reaction. Each idea is explained first, then the tables, counting rules and traps.

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READ ALONGSIDE NCERT XI · Organic Chemistry: Some Basic Principles and Techniques

HOW TO USE THIS SHEET

1. **Skim** — Read the Key ideas, then the formula cards.
2. **Memorise** — Learn the formulas and check every Trap box.
3. **Test** — Do the worked examples, then this chapter's PYQs.
4. **Revise** — Use the last-minute checklist before the exam.

Formula memorise · **Key idea** why it works · **Trap** marks lost here · **PYQ** how it is asked

CHAPTER 14

Basic Principles of Organic Chemistry

NCERT XI · Organic Chemistry: Some Basic Principles and Techniques

Covers: IUPAC nomenclature and functional-group priority · structural, geometrical and optical isomerism and counting · inductive, resonance, electromeric effects and hyperconjugation · carbocations, free radicals, carbanions, carbenes · nucleophiles and electrophiles · aromaticity · acidity and basicity orders · types of organic reaction.

1 Nomenclature and degree of unsaturation

- An IUPAC name has a **parent chain** (longest chain containing the principal functional group), a **suffix** for that group and **prefixes** for substituents. Number the chain to give the principal group the lowest locant, then the multiple bonds, then the substituents (lowest set), and write prefixes **alphabetically** (di, tri, sec, tert are ignored; iso and neo count).
- Only the highest-priority group becomes the suffix; the others are prefixes. Priority: carboxylic acid $>$ sulphonic acid $>$ anhydride $>$ ester $>$ acid halide $>$ amide $>$ nitrile $>$ aldehyde $>$ ketone $>$ alcohol $>$ amine $>$ alkene, alkyne (together named -en-yne). Always prefixes: halo, nitro, alkoxy, alkyl.

COMMON NAMES AND GROUPS TO KNOW

GROUP OR COMPOUND	NAME	GROUP OR COMPOUND	NAME
$C_6H_5^-$	phenyl	$C_6H_5CH_2^-$	benzyl
$CH_2{=}CH^-$	vinyl (ethenyl)	$CH_2{=}CH{-}CH_2^-$	allyl (prop-2-en-1-yl)
$(CH_3)_2CH^-$	isopropyl	$(CH_3)_3C^-$, $(CH_3)_3CCH_2^-$	tert-butyl, neopentyl
benzene-1,2-diol / 1,3- / 1,4-	catechol / resorcinol / hydroquinone	methoxybenzene, aminobenzene	anisole, aniline (the same compound as phenylamine)
methylbenzene, hydroxybenzene	toluene, phenol	$HCHO$, CH_3CHO, CH_3COCH_3	formaldehyde, acetaldehyde, acetone
$HCOOH$, CH_3COOH	formic, acetic acid	CH_3Cl, $CHCl_3$, CCl_4	methyl chloride, chloroform, carbon tetrachloride

DEGREE OF UNSATURATION

$$\text{DBE} = C - \frac{H + X}{2} + \frac{N}{2} + 1$$

each ring or π bond counts 1; O and S are ignored; a benzene ring is 4 (C_6H_6: $6 - 3 + 1 = 4$); C_8H_8: 5

SPECIFIC ROTATION

$$[\alpha] = \frac{\alpha_{obs}}{l\,c}$$

l in dm, c in g mL^{-1}; enantiomeric excess $= \dfrac{[\alpha]_{mix}}{[\alpha]_{pure}} \times 100\%$

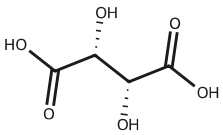
STRUCTURAL ISOMER COUNTS TO MEMORISE

FORMULA	COUNT
C_4H_{10}, C_5H_{12}, C_6H_{14}, C_7H_{16} (alkanes)	2, 3, 5, 9
C_4H_8	alkenes 4 (but-1-ene, cis- and trans-but-2-ene, 2-methylpropene); with two cyclic isomers 6
C_4H_9Cl	4 structural (5 counting the enantiomers of 2-chlorobutane)
$C_4H_{10}O$	4 alcohols + 3 ethers = 7
$C_5H_{10}O$ carbonyls	4 aldehydes + 3 ketones = 7
C_3H_9N	4 amines (1° two, 2° one, 3° one)
C_7H_8O aromatic	5 (*o*-, *m*-, *p*-cresol, benzyl alcohol, anisole)
monochloro products of 2-methylbutane	4 structural isomers (more counting stereoisomers)

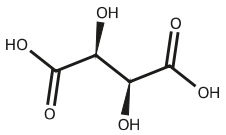
2 Isomerism

TYPES OF STRUCTURAL ISOMERISM

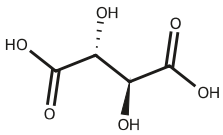
TYPE	MEANING	EXAMPLE
chain	different carbon skeleton	butane and 2-methylpropane
position	same skeleton, group in a different place	propan-1-ol and propan-2-ol
functional group	different functional groups	ethanol and methoxymethane; propanal and propanone
metamerism	different alkyl groups on the same polyvalent atom	$CH_3OC_3H_7$ and $C_2H_5OC_2H_5$
tautomerism	rapid equilibrium, shifting of H (needs an α-H next to C=O)	keto-enol: propanone $\rightleftharpoons$ prop-1-en-2-ol; no tautomerism in benzaldehyde, $HCHO$
ring-chain	ring and open-chain form	C_3H_6: propene and cyclopropane



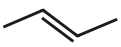
(2R,3R)
dextro / active



(2S,3S)
laevo / active



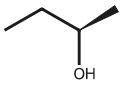
meso (2R,3S)
inactive, internal mirror



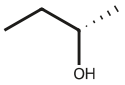
E (trans)-but-2-ene



Z (cis)-but-2-ene



(R)-butan-2-ol



(S)-butan-2-ol

enantiomers: same b.p., m.p.;
rotate plane-polarised light equally,
in opposite senses



propanone

prop-1-en-2-ol
keto-enol tautomers

tartaric acid has two similar stereocentres: (2R,3R) and (2S,3S) are enantiomers, the meso (2R,3S) form has a mirror plane and is inactive: 3 stereoisomers (not 4)

GEOMETRICAL (CIS-TRANS, E-Z)

- Needs restricted rotation (C=C, ring) and two **different** groups on each carbon of the double bond; a terminal $=CH_2$ has none.
- **CIP**: rank the two groups on each carbon by atomic number (then the next atoms); higher-priority groups on the same side is **Z**, opposite is **E**.
- Counts: n unlike C=C: 2^n; symmetric polyene: n even $2^{n-1} + 2^{n/2-1}$, n odd $2^{n-1} + 2^{(n-1)/2}$ (hexa-2,4-diene: 3).

OPTICAL (CHIRALITY)

- A carbon with **four different groups** is a chiral centre; the molecule is optically active if it has no plane or centre of symmetry. Enantiomers: mirror images; diastereomers: stereoisomers that are not mirror images (different physical properties).
- n different chiral centres: 2^n stereoisomers. Symmetric molecule, n even: active 2^{n-1}, meso $2^{n/2-1}$ (tartaric acid: $2 + 1$ meso $= 3$). n odd: active $2^{n-1} - 2^{(n-1)/2}$, meso $2^{(n-1)/2}$.
- **R/S**: lowest-priority group away from the viewer; priorities $1 \to 2 \to 3$ clockwise is R. A racemic mixture (d/l, $50:50$) is inactive by external compensation, a meso compound by internal.

KEY IDEA

Count stereoisomers in this order: (1) find the stereocentres and stereogenic double bonds; (2) look for symmetry (meso); (3) apply 2^n and subtract duplicates. Optical activity needs chirality, not just a chiral centre: a meso compound has chiral centres and is inactive.

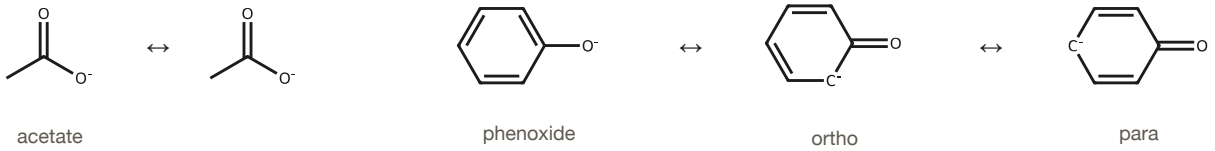
QUICK CHECK

Total stereoisomers of $\mathrm{CH_3CH(OH)CH(OH)CH_3}$ and of $\mathrm{CH_3CH(OH)CH(OH)CH_2CH_3}$?

Answer: First is symmetric, $n = 2$: 2 active + 1 meso $= 3$. Second is unsymmetrical: $2^2 = 4$.

3 Electronic effects

- **Inductive effect** (I): permanent polarisation of a σ bond by the electronegativity of an atom or group; it falls off sharply and is felt for about three carbons. $-I$ groups withdraw electrons; $+I$ groups push. A carbon is more electronegative the more s character: $sp > sp^2 > sp^3$.
- **Resonance (mesomeric) effect** (M): delocalisation of π electrons or lone pairs through a conjugated system. $+M$ groups donate a lone pair into the π system; $-M$ groups pull π density. The real molecule is a **hybrid**, lower in energy than any contributor; the contributors are not in equilibrium.
- **Hyperconjugation**: delocalisation of the σ electrons of a C$-$H bond on an α-carbon into an adjacent empty p orbital or π bond ("no-bond resonance"): the number of hyperconjugative structures equals the number of α-hydrogens. It stabilises alkenes, carbocations and radicals.
- **Electromeric effect**: temporary, appears only in the presence of an attacking reagent, on a multiple bond ($+E$ towards the electrophile, $-E$ away).





-M group pulls charge onto its O, so p-nitrophenol is more acidic

resonance hybrids: the negative charge is shared, so the anion is stabilised (acetate by two equivalent forms, p-nitrophenoxide by delocalisation onto the nitro group)

EFFECTS OF COMMON GROUPS

EFFECT	GROUPS (STRONGEST FIRST WHERE AN ORDER IS KNOWN)
$-I$	$-\mathrm{NR_3^+} > -\mathrm{NO_2} > -\mathrm{CN} > -\mathrm{SO_3H} > -\mathrm{CHO} > -\mathrm{COR} > -\mathrm{COOH} > -\mathrm{F} > -\mathrm{Cl} > -\mathrm{Br} > -\mathrm{I} > -\mathrm{OH} > -\mathrm{OR} > -\mathrm{NH_2} > -\mathrm{C_6H_5} > -\mathrm{H}$
$+I$	$-\mathrm{O^-} > -\mathrm{COO^-} > -\mathrm{C(CH_3)_3} > -\mathrm{CH(CH_3)_2} > -\mathrm{CH_2CH_3} > -\mathrm{CH_3} > -\mathrm{H}$ (and D > H)
$+M$	$-\mathrm{O^-} > -\mathrm{NR_2} \approx -\mathrm{NH_2} > -\mathrm{OH} > -\mathrm{OR} > -\mathrm{NHCOR} > -\mathrm{X}$ (halogens: weak $+M$)
$-M$	$-\mathrm{NO_2}$, $-\mathrm{CN}$, $-\mathrm{CHO}$, $-\mathrm{COR}$, $-\mathrm{COOH}$, $-\mathrm{COOR}$, $-\mathrm{CONH_2}$, $-\mathrm{SO_3H}$

RESONANCE RULES (STABILITY OF CONTRIBUTORS)

- More covalent bonds and complete octets are better; less charge separation is better; negative charge on the more electronegative atom, positive on the less.
- Equivalent contributors (carboxylate, benzene) give a large stabilisation. The hybrid has bond orders between those of the contributors.

TRAP

Halogens: $-I$ outweighs $+M$, so they **deactivate** the ring but direct **ortho/para**. $-OCH_3$ is $-I$ but $+M$: at the meta position only $-I$ acts, so m-methoxybenzoic acid is stronger than benzoic acid, p-methoxy weaker. Aminobenzene and aniline are the same compound.

4 Reactive intermediates and types of reaction

REACTIVE INTERMEDIATES

INTERMEDIATE	SHAPE	STABILITY ORDER	NOTES
carbocation	sp^2, planar, empty p	$(C_6H_5)_3C^+ > (C_6H_5)_2CH^+ >$ benzyl $\approx$ allyl $\approx$ $3^\circ > 2^\circ > 1^\circ > CH_3^+$; $CH_3OCH_2^+$ stabilised by $+M$ of O; vinyl and phenyl cations very unstable	forms by heterolysis; 1, 2-hydride or methyl shifts give a more stable cation
free radical	sp^2, nearly planar	benzyl $\approx$ allyl $> 3^\circ > 2^\circ > 1^\circ > CH_3\cdot >$ vinyl	forms by homolysis (heat, light, peroxide)
carbanion	sp^3 pyramidal	$CH_3^- > 1^\circ > 2^\circ > 3^\circ$ (reverse of carbocation); more stable with s character and $-I/-M$: $HC{\equiv}C^- > CH_2{=}CH^- > CH_3CH_2^-$	forms by deprotonation
carbene (:CR_2)	singlet sp^2 or triplet	electrophilic, neutral divalent C	$CHCl_3 + KOH \rightarrow :CCl_2$ (Reimer-Tiemann, carbylamine)

REACTION TYPES AND THE USUAL EXAMPLES

TYPE	EXAMPLES
nucleophilic substitution	S_N1, S_N2: hydrolysis of R–X, Williamson ether synthesis
electrophilic substitution	nitration, halogenation, sulphonation, Friedel-Crafts of benzene
electrophilic addition	HX, Br_2, H_2O/H^+ to alkenes and alkynes
free-radical substitution	halogenation of alkanes ($Cl_2/h\nu$), allylic bromination (NBS)
nucleophilic addition	HCN, Grignard, $NaHSO_3$, NH_2Z to C=O
elimination	alc. KOH on R–X; acid dehydration of alcohols
rearrangement	pinacol-pinacolone, Hofmann bromamide, carbocation shifts, Beckmann

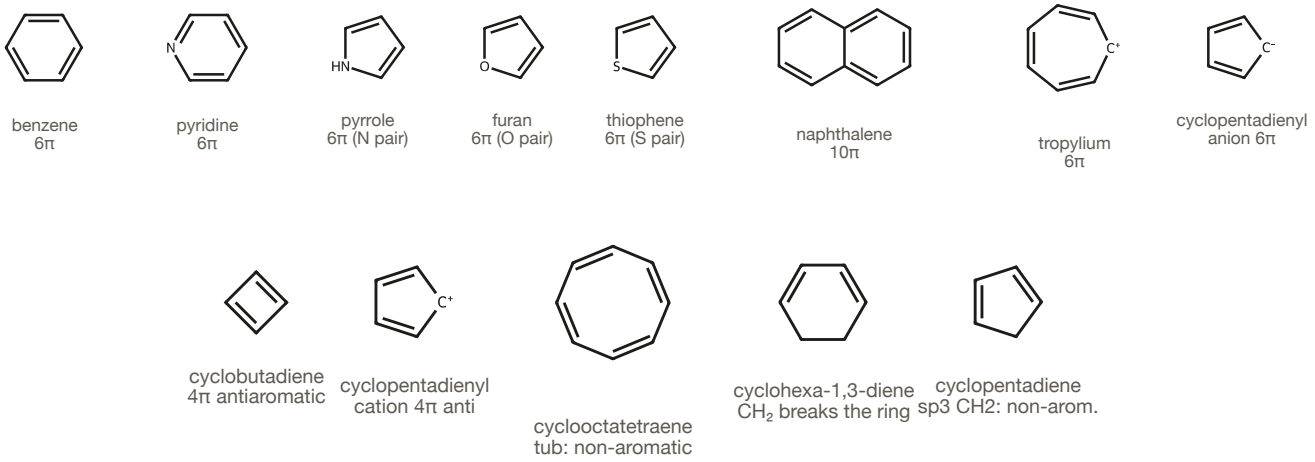
ELECTROPHILES AND NUCLEOPHILES

- **Electrophiles** (electron-pair acceptors): H^+, NO_2^+, Br^+ (from $Br_2/FeBr_3$), R^+, RCO^+, SO_3, BF_3, $AlCl_3$, carbonyl carbon.
- **Nucleophiles** (donors): OH^-, RO^-, CN^-, X^-, RS^-, H_2O, ROH, NH_3, amines, C=C (weak).
- Same attacking atom: nucleophilicity follows basicity, $RO^- > HO^- > RCOO^- > ROH$. Protic solvents: $I^- > Br^- > Cl^- > F^-$ (small ions are solvated); polar aprotic (DMSO, DMF): $F^- > Cl^- > Br^- > I^-$.

WHY IT WORKS

The stability of the intermediate decides the reaction. More hyperconjugation (more α-H) and more resonance mean a more stable carbocation or radical, so they drive S_N1, E1, Markovnikov addition and easy dehydration. A carbocation is stabilised by electron donation; a carbanion by electron withdrawal: opposite trends.

5 Aromaticity, acidity and basicity



Hückel: aromatic needs a cyclic, planar, fully conjugated ring with (4n+2) π electrons; 4n π electrons make it antiaromatic

ACIDITY ORDERS

SERIES	ORDER AND REASON
general	$RSO_3H > RCOOH > C_6H_5OH > H_2O > ROH > HC{\equiv}CH > NH_3 > CH_2{=}CH_2 > CH_3CH_3$
carboxylic acids	$HCOOH > CH_3COOH > CH_3CH_2COOH$ (+I of alkyl lowers acidity; the textbook order continues with larger alkyl groups)
haloacids	$FCH_2COOH > ClCH_2COOH > BrCH_2COOH > ICH_2COOH$; $Cl_3CCOOH > Cl_2CHCOOH > ClCH_2COOH$; nearer to COOH is stronger (2-chloro > 3- > 4-chlorobutanoic)
benzoic acids	p-nitro > m-nitro > benzoic (pK_a 4.2) > p-methyl > p-methoxy; benzoic > acetic (4.76); ortho substituents (nearly any) raise acidity
phenols	picric acid $\gg$ 2,4-dinitrophenol > p-nitrophenol > o-nitrophenol (intramolecular H bond) > m-nitrophenol > phenol > cresols; p-chlorophenol > phenol
alcohols	methanol > $1^\circ > 2^\circ > 3^\circ$ (more alkyl groups: $+I$ and poorer solvation of the alkoxide)
C−H acids	terminal alkyne (pK_a about 25) reacts with Na, $NaNH_2$, ammoniacal $AgNO_3$; 1,3-dicarbonyl CH_2 (9 to 13)

BASICITY (AQUEOUS AMINES; DETAILS IN THE NITROGEN SHEET)

ORDER	REMARK
$(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$; $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$	balance of +I, solvation and sterics
aliphatic amine > NH_3 > aniline > diphenylamine > triphenylamine	aryl groups delocalise the lone pair
pyridine (pK_b about 8.8) > aniline (9.4); pyrrole is not basic	lone pair of pyrrole is part of the aromatic sextet
guanidine	strongest neutral organic base: resonance-stabilised cation

TRAP

Cyclooctatetraene is non-aromatic (tub-shaped, not planar), not antiaromatic. Heteroatoms: S is in thiophene, cysteine and methionine; O in furan; N in pyridine and pyrrole. A cyclopentadiene CH_2 ring is non-aromatic; its anion is aromatic (hence cyclopentadiene is a strong carbon acid, $pK_a \approx 16$).

QUICK CHECK

Which is more acidic: p-nitrophenol or m-nitrophenol? CH_3COOH or $ClCH_2COOH$?

Answer: p-nitrophenol ($-M$ and $-I$ both act at para). $ClCH_2COOH$ ($-I$ of Cl stabilises the anion).

6 Worked examples

DEGREE OF UNSATURATION

DBE of $C_7H_7NO_2$ (nitrotoluene) and of C_4H_8O?

$C_7H_7NO_2$: $7 - \frac{7}{2} + \frac{1}{2} + 1 = 5$ (ring 4 + N=O 1); C_4H_8O : $4 - 4 + 1 = 1$ (one ring or C=O)

OPTICAL ISOMERS

Total stereoisomers of 2,3,4-trihydroxypentanedioic acid ($HOOC(CHOH)_3COOH$, symmetric).

$n = 3$ odd: active $2^2 - 2^1 = 2$, meso $2^1 = 2$; total 4

GEOMETRICAL ISOMERS

Geometrical isomers of hexa-2,4-diene and of 3-methylpent-2-ene.

hexa-2,4-diene is symmetric, $n = 2$: $2^1 + 2^0 = 3$ (EE, ZZ, EZ); 3-methylpent-2-ene: ends differ (CH_3/H and CH_3/C_2H_5): 2

STABILITY ORDER

Order the carbocations $CH_3CH_2^+$, $(CH_3)_2CH^+$, $C_6H_5CH_2^+$, $CH_2{=}CH^+$.

$C_6H_5CH_2^+ > (CH_3)_2CH^+ > CH_3CH_2^+ > CH_2{=}CH^+$ (resonance, then hyperconjugation 6 vs 3 α-H, then vinyl worst)

ALKENE STABILITY

Order by stability: 2-methylbut-2-ene, cis-but-2-ene, propene, 2,3-dimethylbut-2-ene.

more alkyl groups on the double bond means more hyperconjugation: $2,3$-dimethylbut-2-ene $>$ 2-methylbut-2-ene $>$ cis-but-2-ene $>$ propene (trans $>$ cis for the same substitution)

AROMATIC COUNT

How many of benzene, pyridine, pyrrole, cyclobutadiene, tropylium cation, cyclooctatetraene are aromatic?

benzene, pyridine, pyrrole, tropylium: 4 (6π each); cyclobutadiene antiaromatic; cyclooctatetraene non-aromatic

7 Last-minute checklist

BEFORE YOU ANSWER

Name the effect (I, M, hyperconjugation) and the direction. For stability, always look at the intermediate or the conjugate base. Count stereocentres first, then check symmetry.

- DBE $= C - \frac{H+X}{2} + \frac{N}{2} + 1$; chiral centre needs 4 different groups; 2^n stereoisomers, meso reduces it; E/Z by CIP; geometrical isomerism needs two different groups on each C.
- $-I$: $NR_3^+ > NO_2 > CN > COOH > F > Cl > OH$; $+I$: $tert{-}Bu > iPr > Et > Me$; halogens: $-I > +M$ (deactivating, o/p); OH, OR, NH_2: $+M > -I$.
- Carbocation: $3^\circ > 2^\circ > 1^\circ$, benzyl and allyl highest; radical same; carbanion reverse; alkene stability by number of α-H; heat of hydrogenation lower is more stable.
- Aromatic: cyclic, planar, conjugated, $4n + 2$ π electrons; tropylium, cyclopentadienyl anion aromatic; cyclobutadiene antiaromatic; cyclooctatetraene non-aromatic.
- Acidity: carboxylic $>$ phenol $>$ alcohol; $-I/-M$ raises, $+I$ lowers; o-nitrophenol is less acidic than p (intramolecular H bond); aliphatic amine $>$ NH_3 $>$ aniline.

Now test it. Practise this chapter with past-paper and bank questions on Prep Vault. **Practice this chapter →**