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CH 05

Substitution & Elimination — SN1, SN2, E1 and E2

05

Decide between SN1, SN2, E1 and E2 from the substrate, reagent, solvent and temperature — with stereochemistry, rearrangements, Saytzeff versus Hofmann, ambident nucleophiles, an exam trap gallery, graded MCQs and a one-page revision sheet.

WHAT YOU WILL BE ABLE TO DO

- Write the mechanism, rate law and stereochemical result of SN1, SN2, E1 and E2
- Rank substrates, leaving groups and nucleophiles for each pathway, and explain the role of solvent
- Predict carbocation rearrangements (hydride and methyl shifts) and their products
- Choose the major alkene by Saytzeff's or Hofmann's rule, including anti-periplanar E2
- Predict products of ambident nucleophiles (KCN/AgCN, KNO_2/$AgNO_2$) and explain why aryl halides resist substitution

INSIDE

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G Choosing the pathway
H Special substrates

HOW TO USE THESE NOTES

IN ONE LINE The core idea of a section	**KEY IDEA** The concept to remember	**EXAM TRAP** Where marks are usually lost
SOLVED EXAMPLE Worked step by step	**CHECK YOURSELF** Quick self-test	**MEMORY HOOK** A line that sticks

SECTION A

The big picture

A

Four questions, asked in this order, decide the path.

IN ONE LINE

The substrate (methyl, 1°, 2°, 3°), the reagent (strong or weak, small or bulky, nucleophile or base), the solvent (protic or aprotic) and the temperature together decide between SN1, SN2, E1 and E2.

1. **What is the substrate?** Methyl and 1° favour SN2; 3° cannot do SN2.
2. **What is the reagent?** Strong nucleophile → SN2; strong base → E2; weak nucleophile/base → SN1 or E1.
3. **What is the solvent?** Polar aprotic speeds SN2; polar protic stabilises ions and favours SN1/E1.
4. **Is it heated?** Heat favours elimination over substitution.

THINK OF IT LIKE THIS

SN2 is a hold-up at a narrow doorway: the nucleophile pushes in from the back while the leaving group walks out the front, all in one move — crowding blocks it. SN1 is a two-step queue: the leaving group leaves first, the carbocation waits, and anyone can come in from either side.

	SN2	SN1	E2	E1
Steps	One (concerted)	Two (via carbocation)	One (concerted)	Two (via carbocation)
Rate law	k[RX][Nu^-]	k[RX]	k[RX][B^-]	k[RX]
Best substrate	CH_3 > 1° > 2°	3° > 2°; benzylic, allylic	3° > 2° > 1°	3° > 2°
Reagent	Strong nucleophile	Weak nucleophile	Strong base	Weak base
Solvent	Polar aprotic	Polar protic	—	Polar protic
Stereo / product	Inversion	Racemisation (mostly)	Anti-periplanar; Saytzeff	Saytzeff

	SN2	SN1	E2	E1
Rearrangement	Never	Possible	Never	Possible

SECTION B

B

SN2 — bimolecular substitution

One step, backside attack, inversion.

The nucleophile attacks the carbon from the side opposite the leaving group. In the transition state the carbon is partly bonded to both (five groups around it, trigonal bipyramidal). As the leaving group departs the other three groups flip over, like an umbrella in the wind.

$$\text{Rate} = k\,[RX]\,[Nu^-]$$

Second order — doubling either concentration doubles the rate

KEY IDEA

SN2 always gives inversion of configuration (Walden inversion). (R)-2-bromobutane with OH^- by SN2 gives (S)-butan-2-ol. If the nucleophile changes the priority order, the label may not flip even though the geometry does — check priorities each time.

- **Reactivity:** CH_3X > 1° > 2° ≫ 3° (3° does not react by SN2). Bulky groups block the back side.
- **Neopentyl bromide** $(CH_3)_3CCH_2Br$ is a 1° halide yet reacts extremely slowly by SN2 — the tert-butyl group next door blocks the attack.
- **Polar aprotic solvents** (DMSO, DMF, acetone) speed SN2: they solvate the cation but leave the anion "naked" and reactive.
- **Finkelstein reaction:** R–Cl + NaI in dry acetone → R–I + NaCl↓. NaCl is insoluble in acetone, which pulls the equilibrium forward.

SOLVED EXAMPLE 01 — STEREOCHEMISTRY OF SN2

(R)-2-bromobutane reacts with NaOH in acetone. Name the product with its configuration.

SOLUTION

1. A 2° halide, strong nucleophile, polar aprotic solvent → SN2.
2. OH^- attacks from the back side; the configuration inverts.
3. OH takes the place of Br in the priority order (both are highest), so the label flips too.

ANSWER (S)-butan-2-ol.

SECTION C

SN1 — unimolecular substitution

C

Two steps, a flat carbocation, a mixture of products.

1. **Slow step:** R–X → $R^+ + X^-$ (ionisation; this step fixes the rate).
2. **Fast step:** $R^+ + Nu^-$ → R–Nu.

$$\text{Rate} = k[RX]$$

First order — the nucleophile is not in the rate law; adding more of it does not speed the reaction

- **Reactivity follows carbocation stability:** 3° > 2° > 1° > CH_3. Benzylic and allylic cations (resonance-stabilised) also react fast.
- **Polar protic solvents** (water, alcohols, formic acid) stabilise both the carbocation and the leaving anion. Reactions in water or alcohol as solvent are called **solvolysis**.
- **Stereochemistry:** the carbocation is planar (sp^2) and can be attacked from either face → **racemisation**. In practice there is slightly more inversion, because the departing X^- briefly shields its own face.
- **Rearrangement:** a less stable carbocation shifts H^- or CH_3^- from the next carbon to become more stable (2° → 3°).

SOLVED EXAMPLE 02 — HYDRIDE SHIFT

Predict the main product when 3-methylbutan-2-ol reacts with HBr.

SOLUTION

1. Protonation and loss of water gives a 2° carbocation at C2.
2. A hydride shifts from C3 to C2, giving a more stable 3° carbocation at C3.
3. Br^- attacks the 3° carbocation.

ANSWER 2-Bromo-2-methylbutane (not 2-bromo-3-methylbutane).

SOLVED EXAMPLE 03 — METHYL SHIFT

Neopentyl bromide is heated in water. What is the main substitution product?

SOLUTION

1. SN2 is blocked by the tert-butyl group; slow ionisation gives a very unstable 1° carbocation.
2. A methyl group shifts to form the 3° 2-methylbut-2-yl cation.
3. Water attacks the 3° carbocation; loss of H^+ gives the alcohol.

ANSWER 2-Methylbutan-2-ol (with some alkene by E1).

CHECK YOURSELF

C1 Which reacts faster by SN1: benzyl chloride or chlorobenzene?

C2 What happens to the SN1 rate if [Nu^-] is doubled?

Answers at the end of the chapter.

SECTION D

D

Leaving groups and nucleophiles

Who leaves easily, and who attacks well.

Leaving group ability

A good leaving group is a **weak base** — stable once it has left with the electron pair. I^- > Br^- > Cl^- > F^-. So reactivity is R–I > R–Br > R–Cl > R–F for both SN1 and SN2. OH^- is a poor leaving group, which is why alcohols need acid first (to make H_2O the leaving group).

Nucleophilicity

Rule	Order	Reason
Same attacking atom	RO^- > HO^- > ROH; NH_2^- > NH_3	Negative charge increases nucleophilicity
Across a period	CH_3^- > NH_2^- > OH^- > F^-	Less electronegative atom holds electrons less tightly
Down a group, polar protic solvent	I^- > Br^- > Cl^- > F^-	Small F^- is heavily H-bonded and caged by the solvent
Down a group, polar aprotic solvent	F^- > Cl^- > Br^- > I^-	Ions are free; basicity decides
Bulk	CH_3O^- > $(CH_3)_3CO^-$	tert-Butoxide is a strong base but a poor nucleophile

Ambident nucleophiles

Reagent	Bond type	Attacking atom	Product with R-X
KCN	Mainly ionic	C (the more nucleophilic end)	Alkyl cyanide R–C≡N
AgCN	Mainly covalent (Ag–C)	N (C is tied up)	Alkyl isocyanide R–N≡C
KNO_2	Ionic	O	Alkyl nitrite R–O–N=O
$AgNO_2$	Covalent	N	Nitroalkane R–NO_2

KEY IDEA

K gives the "normal" atom, Ag forces the other one. With KCN and KNO_2 the free ion attacks through C and O respectively; the silver salts are covalent, so the bound atom can't attack and the other end does.

SECTION E

E2 — bimolecular elimination

E

One step, a strong base, and a strict geometry rule.

The base removes a β-hydrogen while the C–X bond breaks and the C=C forms, all at once. Strong bases favour it: alcoholic KOH, NaOEt in ethanol, t-BuOK.

$$\text{Rate} = k\,[RX]\,[B^-]$$

Second order

KEY IDEA

Anti-periplanar requirement: the β-H and the leaving group must be on opposite sides, in one plane (dihedral angle 180°). In a cyclohexane ring both must be axial — if no axial β-H sits anti to an axial X, E2 cannot happen from that conformation.

Which alkene? Saytzeff versus Hofmann

- **Saytzeff (Zaitsev) rule:** with a small base, the more substituted (more stable) alkene is major. 2-Bromobutane + alc. KOH → but-2-ene (mainly trans) > but-1-ene.
- **Hofmann product:** a bulky base such as t-BuOK removes the more accessible H on the less substituted carbon → the less substituted alkene is major.
- Hofmann elimination of quaternary ammonium hydroxides also gives the less substituted alkene.

SOLVED EXAMPLE 04 — BASE SIZE CHANGES THE PRODUCT

Give the major alkene from 2-bromo-2-methylbutane with (a) NaOEt in ethanol, (b) t-BuOK.

SOLUTION

1. Two kinds of β-H: on CH_3 (gives a terminal alkene) and on CH_2 (gives an internal alkene).
2. (a) Small base: Saytzeff → the more substituted alkene.
3. (b) Bulky base: attacks the less hindered CH_3 hydrogens → Hofmann.

ANSWER (a) 2-Methylbut-2-ene. (b) 2-Methylbut-1-ene.

SECTION F

E1 — unimolecular elimination

F

The carbocation loses a proton instead of gaining a nucleophile.

- Same first step as SN1: R–X → $R^+ + X^-$ (slow). Then a weak base (often the solvent) removes a β-H.
- Rate = k[RX]. Favoured by 3° substrates, weak bases, polar protic solvents and **heat**.
- Always competes with SN1; higher temperature shifts the balance toward elimination.
- Gives the Saytzeff product and can rearrange, just like SN1.
- Acid-catalysed dehydration of alcohols (conc. H_2SO_4, heat) is an E1 reaction for 2° and 3° alcohols: ease 3° > 2° > 1°.

CHECK YOURSELF

C3 Why does t-BuOK favour elimination over substitution?

C4 Which alkene is major when 2-bromobutane is heated with alcoholic KOH?

Answers at the end of the chapter.

SECTION G

Choosing the pathway

G

The decision table most questions reduce to.

Substrate	Strong nucleophile, weak base (I^-, CN^-, RS^-, N_3^-)	Strong base (OH^-, RO^-)	Bulky strong base (t-BuO^-)	Weak nucleophile/base (H_2O, ROH)
CH_3X	SN2	SN2	SN2	No reaction (slow)
1°	SN2	SN2 (E2 if heated)	E2	Very slow
2°	SN2	E2 mainly	E2	SN1 / E1 (slow)
3°	SN1 / E1	E2	E2	SN1 (cold) / E1 (heat)

- **Aqueous KOH** → substitution (alcohol). **Alcoholic KOH** → elimination (alkene). The ethoxide formed in ethanol is a stronger base, and alcohol solvates OH^- less.
- Higher temperature always increases the proportion of elimination.

SOLVED EXAMPLE 05 — AQUEOUS VS ALCOHOLIC

2-Bromopropane is treated with (a) aqueous KOH, (b) alcoholic KOH and heat. Give the main products.

SOLUTION

1. (a) Water as solvent, OH^- as nucleophile, no heat → substitution.
2. (b) Alcoholic medium, heat → E2 elimination.

ANSWER (a) Propan-2-ol. (b) Propene.

SECTION H

Special substrates

H

Where the rules above need a second look.

- **Allylic and benzylic halides** are very reactive by both SN1 (resonance-stabilised cation) and SN2 (the π system stabilises the transition state).
- **Vinyl and aryl halides** (C–X on an sp^2 carbon) resist nucleophilic substitution: the C–X bond has partial double-bond character from resonance, the sp^2 carbon holds the bond more tightly, the phenyl cation is very unstable, and the ring's π cloud repels the nucleophile.
- Aryl halides react under harsh conditions (Dow process: NaOH at 623 K, high pressure) or when **electron-withdrawing groups sit ortho or para** to X: 2,4,6-trinitrochlorobenzene is hydrolysed by warm water.
- A meta nitro group has little effect: it cannot delocalise the negative charge of the intermediate.

KEY IDEA

Order of reactivity toward aqueous hydrolysis: 2,4,6-trinitrochlorobenzene > 2,4-dinitrochlorobenzene > 4-nitrochlorobenzene > chlorobenzene. Each o/p nitro group stabilises the negative intermediate by resonance.

SECTION I

Exam trap gallery

I

Where marks are lost in this chapter.

✗ TRAP 01 · WHAT STUDENTS WRITE

SN1 gives complete inversion.

✓ WHAT IS ACTUALLY CORRECT

SN2 gives inversion; SN1 gives mostly racemisation (slight excess inversion).

WHY A planar carbocation can be attacked from both faces.

✗ TRAP 02 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
Increasing [Nu^-] speeds up SN1.	SN1 rate = k[RX] only.

WHY The nucleophile enters after the slow step.

✗ TRAP 03 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
3° halides react fastest by SN2.	3° halides do not react by SN2.

WHY Three alkyl groups block backside attack.

✗ TRAP 04 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
Neopentyl bromide reacts fast by SN2 because it is 1°.	It is extremely slow by SN2.

WHY The neighbouring tert-butyl group blocks the back side.

✗ TRAP 05 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
KCN and AgCN both give alkyl cyanides.	KCN → R–CN; AgCN → R–NC (isocyanide).

WHY Ag–C bond in AgCN leaves N to attack.

✗ TRAP 06 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
Aqueous and alcoholic KOH give the same product.	Aqueous → alcohol; alcoholic → alkene.

WHY Ethoxide in ethanol is a strong base; heat favours E2.

✗ TRAP 07 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
t-BuOK gives the Saytzeff alkene.	t-BuOK gives the Hofmann (less substituted) alkene.

WHY A bulky base takes the most accessible hydrogen.

✗ TRAP 08 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
3-Methylbutan-2-ol + HBr gives 2-bromo-3-methylbutane.	Main product: 2-bromo-2-methylbutane.

WHY 2° cation rearranges to 3° by a hydride shift.

✗ TRAP 09 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
In polar protic solvents F^- is the best nucleophile among the halides.	In protic solvents I^- is best; F^- is best only in aprotic solvents.

WHY H bonding cages the small F^- ion.

MEMORY HOOK

"SN2: two in the rate, turns it inside-out" — second order, inversion.

"SN1: one in the rate, flat in between" — first order, planar carbocation, racemisation.

"Small base Saytzeff, big base Hofmann."

"Water substitutes, alcohol eliminates" — aqueous vs alcoholic KOH.

SECTION J

Practice MCQs

J

Levels: Easy, Moderate, Tough.

Q01 The rate of an SN2 reaction depends on: [EASY]

(a) [RX] only
(b) [Nu^-] only
(c) both [RX] and [Nu^-]
(d) neither

Q02 Which reacts fastest by SN2? [EASY]

(a) CH_3Br
(b) $(CH_3)_2CHBr$
(c) $(CH_3)_3CBr$
(d) $(CH_3)_3CCH_2Br$

Q03 Which reacts fastest by SN1? [EASY]

(a) CH_3Cl
(b) CH_3CH_2Cl
(c) $(CH_3)_2CHCl$
(d) $(CH_3)_3CCl$

Q04 The best leaving group is: [EASY]

(a) F^-
(b) Cl^-
(c) Br^-
(d) I^-

Q05 Ethyl bromide with alcoholic KOH mainly gives: [EASY]

(a) ethanol
(b) ethene
(c) diethyl ether
(d) ethane

Q06 An alkyl halide reacts with AgCN to give mainly: [MODERATE]

(a) alkyl cyanide
(b) alkyl isocyanide
(c) carboxylic acid
(d) amine

Q07 A nitroalkane is the main product when R–X reacts with: [MODERATE]

(a) KNO_2
(b) $AgNO_2$
(c) $NaNO_3$
(d) HNO_2

Q08 SN1 reaction of an optically active 2° halide gives: [MODERATE]

(a) complete retention
(b) complete inversion
(c) racemisation (with some excess inversion)
(d) no reaction

Q09 Which solvent best speeds an SN2 reaction of NaCN with CH_3CH_2Br? [MODERATE]

(a) water (b) ethanol
(c) DMSO (d) acetic acid

Q10 2-Bromobutane with alcoholic KOH gives as major product: [MODERATE]

(a) but-1-ene (b) but-2-ene
(c) butan-2-ol (d) butane

Q11 Chlorobenzene is less reactive than chloroethane toward nucleophiles because: [MODERATE]

(a) C–Cl bond has partial double-bond character (b) Cl is more electronegative in chlorobenzene
(c) benzene is a stronger acid (d) chlorobenzene is non-polar

Q12 Which is hydrolysed most easily? [MODERATE]

(a) chlorobenzene (b) 4-nitrochlorobenzene
(c) 3-nitrochlorobenzene (d) 2,4-dinitrochlorobenzene

Q13 2-Bromo-2-methylbutane with t-BuOK gives mainly: [TOUGH]

(a) 2-methylbut-2-ene (b) 2-methylbut-1-ene
(c) 2-methylbutan-2-ol (d) 3-methylbut-1-ene

Q14 3-Methylbutan-2-ol with HBr gives mainly: [TOUGH]

(a) 2-bromo-3-methylbutane (b) 1-bromo-3-methylbutane
(c) 2-bromo-2-methylbutane (d) 3-methylbut-1-ene

Q15 For E2 in a cyclohexyl halide, the H and the leaving group must be: [TOUGH]

(a) both equatorial (b) both axial and anti
(c) cis and equatorial (d) one axial, one equatorial on the same side

Answer key with explanations

Q01 **(c) both [RX] and [Nu^-]** — Bimolecular, one step.

Q02 **(a) CH_3Br** — Least hindered.

Q03 **(d) $(CH_3)_3CCl$** — Most stable 3° carbocation.

Q04 **(d) I^-** — Weakest base.

Q05 **(b) ethene** — Alcoholic KOH → elimination.

Q06 **(b) alkyl isocyanide** — Attack through N.

Q07 **(b) $AgNO_2$** — Covalent $AgNO_2$ attacks through N.

Q08 **(c) racemisation (with some excess inversion)** — Planar carbocation.

Q09 **(c) DMSO** — Polar aprotic.

Q10 **(b) but-2-ene** — Saytzeff.

Q11 **(a) C–Cl bond has partial double-bond character** — Resonance with the ring.

Q12 **(d) 2,4-dinitrochlorobenzene** — Two o/p nitro groups.

Q13 **(b) 2-methylbut-1-ene** — Bulky base → Hofmann.

Q14 **(c) 2-bromo-2-methylbutane** — Hydride shift to 3° cation.

Q15 **(b) both axial and anti** — Anti-periplanar = trans-diaxial.

SECTION K

Advanced problems

K

Each needs two ideas from the chapter.

SOLVED EXAMPLE 06 — RATE CHANGE

The reaction of $(CH_3)_3CBr$ with water is run with $[(CH_3)_3CBr]$ doubled and an added nucleophile (OH^-) at double concentration. By what factor does the rate change?

SOLUTION

1. 3° substrate, water as solvent → SN1.
2. Rate = k[RX]: doubling [RX] doubles the rate.
3. $[Nu^-]$ does not appear in the rate law.

ANSWER The rate doubles.

SOLVED EXAMPLE 07 — WHICH SIDE WINS?

Ethyl bromide is treated with (a) NaOEt in ethanol at room temperature, (b) t-BuOK. Predict the main products.

SOLUTION

1. (a) 1° substrate, small strong nucleophile/base, no heat → SN2.
2. (b) Bulky base cannot reach the back side easily → E2.

ANSWER (a) Diethyl ether (Williamson synthesis). (b) Ethene.

Check-yourself answers

C1 Benzyl chloride: its benzylic carbocation is resonance-stabilised; chlorobenzene does not ionise.

C2 No change — $[Nu^-]$ is not in the SN1 rate law.

C3 It is a strong base but too bulky to reach the carbon for backside attack, so it removes a β-H instead.

C4 But-2-ene (mainly trans), by Saytzeff's rule.

QUICK REVISION

One-page revision

Read this page the night before the exam.

SN2

- Rate = k[RX][Nu^-]; one step
- Backside attack → inversion
- CH_3 > 1° > 2° ≫ 3°; neopentyl very slow
- Polar aprotic (DMSO, DMF, acetone)

SN1

- Rate = k[RX]; carbocation
- 3° > 2°; benzylic, allylic fast
- Racemisation (slight excess inversion)
- Rearranges: H or CH_3 shift to 3°

Leaving groups and nucleophiles

- I^- > Br^- > Cl^- > F^- leaving
- Protic: I^- best Nu; aprotic: F^- best
- KCN → RCN; AgCN → RNC
- KNO_2 → R–ONO; $AgNO_2$ → R–NO_2

E2

- Rate = k[RX][B^-]; strong base
- Anti-periplanar (trans-diaxial in rings)
- Small base: Saytzeff
- Bulky t-BuOK: Hofmann

E1 and choice

- Carbocation, weak base, heat
- Competes with SN1; heat → E1
- Aq. KOH → alcohol; alc. KOH → alkene
- 3° + strong base → E2

Special substrates

- Allylic, benzylic: fast by SN1 and SN2
- Aryl, vinyl: unreactive (partial C=X)
- o/p NO_2 activates aryl halides
- Dow process: 623 K, high pressure

END OF NOTES · RAMGOVINDYADAV.COM