Mechanism of Organic Reactions

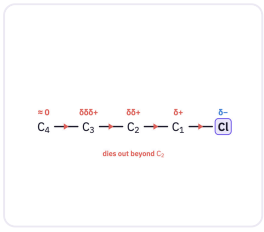
Last-minute revision: the key ideas, standard results and traps of every part. The formula sheet is the last page.

If you only have five minutes

1. Inductive effect: permanent σ polarisation, negligible beyond the second carbon; −I groups strengthen acids, +I groups weaken them.
2. Mesomeric (resonance) effect works through π systems and usually beats −I/+I; electromeric effect is temporary, on demand of a reagent.
3. Hyperconjugation: more α-H, more stabilisation (Baker–Nathan order for alkyl groups).
4. Carbocations (sp^2, planar) and radicals: 3° > 2° > 1° > CH_3; carbanions (sp^3, pyramidal) the reverse; benzyl and allyl are resonance-stabilised.
5. Singlet carbenes add stereospecifically; triplets (diradicals) do not. Benzyne gives cine-substitution.
6. SN2: one step, inversion, CH_3 > 1° > 2° > 3°. SN1: carbocation, racemisation, rearrangement, 3° > 2° > 1°; polar protic solvents favour SN1.
7. Electrophilic addition: Markovnikov via the more stable cation; Br_2 adds anti; peroxide effect only for HBr.
8. Elimination: E1 (cation), E1cB (carbanion), E2 (one step, anti-periplanar); Saytzeff unless the base is bulky (Hofmann).

1 Inductive Effect: −I and +I Groups

- Inductive effect: permanent σ-bond polarisation relayed along the chain; arrowhead mid-bond.
- Partial and short-range: negligible beyond the second carbon.



- −I pulls harder than H, +I pushes harder; +I grows with branching; phenyl and vinyl are weakly −I.

STANDARD RESULTS

−I: NO_2 > CN > COOH > F > Cl > Br > I > OH > C_6H_5.

+I: $(CH_3)_3C-$ > $(CH_3)_2CH-$ > CH_3CH_2- > CH_3- > D > H.

TRAPS

✕ **Thinking the inductive effect moves electrons completely or carries along the whole chain** It is a partial displacement and dies out after about two carbons.

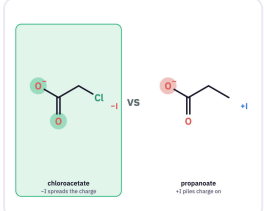
✕ **Calling phenyl and vinyl +I groups** In this series they are weakly −I: an sp^2 carbon is more electronegative.

✕ **Forgetting deuterium** D is slightly +I compared with H.

✕ **Assuming dipole moment follows bond length** CH_3Cl has the largest dipole of the methyl halides although C–Cl is the shortest bond.

2 Acid Strength: pKa and Carboxylic Acids

- $pK_a = -\log K_a$: lower pK_a, stronger acid; stronger acid, weaker conjugate base.
- Acid strength follows carboxylate stability: −I spreads the charge, +I concentrates it.



- More halogens and nearer halogens give stronger acids; α > β > γ.

STANDARD RESULTS

$Cl_3CCOOH > Cl_2CHCOOH > ClCH_2COOH > HCOOH > C$.

$FCH_2COOH > ClCH_2COOH > BrCH_2COOH > ICH_2COOH$.

TRAPS

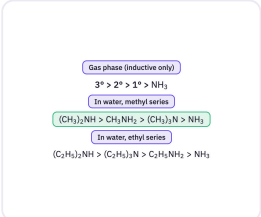
✕ **Reading a bigger pKa as a stronger acid** The scale is logarithmic and inverted: lower pK_a means stronger.

✕ **Ranking halo-acids by halogen size** Rank by electronegativity: F is the strongest −I, so FCH_2COOH is the strongest.

✕ **Putting acetic acid above formic acid** HCOOH has no +I alkyl group, so it is the stronger acid (3.77 vs 4.76).

3 Acidity of Alcohols and Hydrocarbons, Basicity of Amines

- Phenol > water > alcohols; more alkyl groups, weaker O–H acid.
- More s-character, more acidic C–H: sp > sp^2 > sp^3.
- Amines: +I raises basicity; in water, solvation of the cation reorders them; aryl groups lower basicity.



STANDARD RESULTS

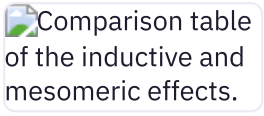
Water, methyl:
$(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$.

Water, ethyl:
$(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$.

TRAPS

- ✕ **Applying the gas-phase order 3° > 2° > 1° to aqueous amines** In water, steric and solvation factors push the 3° amine down.
- ✕ **Using the same aqueous order for the methyl and ethyl series** Methyl: $R_2NH > RNH_2 > R_3N$; ethyl: $R_2NH > R_3N > RNH_2$.
- ✕ **Assuming acidity along a group follows electronegativity** Down a group acidity rises (HF → HI) as the H–X bond gets longer and weaker.

4 Electromeric and Mesomeric (Resonance) Effects



- Electromeric effect: temporary, complete transfer of a π pair while the reagent is present; +E towards the reagent, −E away.
- Mesomeric effect: permanent polarity through conjugation (π–π or π–lone pair); +M gives, −M takes.
- +M groups activate o/p, −M groups deactivate and direct meta; halogens are o/p-directing but deactivating.

STANDARD RESULTS

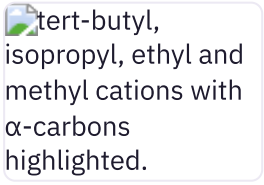
Propene + H^+ → $CH_3–\overset{+}{C}H–CH_3$ (+E).

Vinyl chloride: $Cl^+=CH–CH_2^-$ form; +M > −I.

TRAPS

- ✕ **Calling the electromeric effect permanent** It exists only while the reagent is present.
- ✕ **Drawing a mesomeric arrow from an atom with no π bond or lone pair** Arrows start only from π bonds or lone pairs.
- ✕ **Saying the mesomeric effect fades with distance like the inductive effect** It is transmitted along the full conjugated chain.
- ✕ **Assuming every o/p director activates the ring** Halogens direct o/p yet deactivate (−I wins).

5 Hyperconjugation and the Baker–Nathan Effect



- Hyperconjugation: α C–H σ electrons delocalise into a π bond, empty p or odd-electron orbital (no-bond resonance).
- Number of forms = number of α-H; tert-butyl on a double bond has none.
- Explains alkene stability (basis of Saytzeff), 3° > 2° > 1° cations and radicals, shorter bonds next to π systems.

STANDARD RESULTS

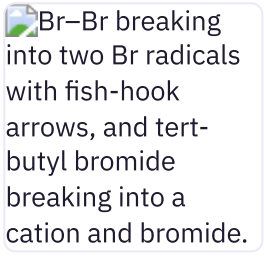
Heats of hydrogenation: ethene 32.8 > propene 30.1 > cis 28.6 > trans 27.6 > 2-methylbut-2-ene 26.9 kcal/mol.

$(CH_3)_2C=C(CH_3)_2$ (12 α-H) > $(CH_3)_2C=CHCH_3$ (9) > $(CH_3)_2C=CH_2$ (6).

TRAPS

- ✕ **Counting H atoms that are not on the α-carbon** Only the carbon attached to the sp^2 (or cationic, radical) carbon counts.
- ✕ **Thinking a tert-butyl group shows hyperconjugation** Its α-carbon has no H. (The tert-butyl cation is different: its α-carbons are the methyls, 9 α-H.)
- ✕ **Reading a larger heat of hydrogenation as more stable** More heat released means a higher-energy, less stable alkene.

6 Bond Fission and Free Radicals



- Homolysis gives radicals (fish-hook arrows); heterolysis gives ions, the pair going to the more electronegative atom.
- Lower C–H bond energy, more stable radical.
- Radicals: neutral, paramagnetic, planar sp^2 ($CF_3•$ pyramidal); react by combining, attacking, or losing a small molecule.

STANDARD RESULTS

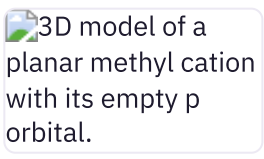
Allyl ≈ benzyl > 3° > 2° > 1° > $CH_3•$ > vinyl.

102 − 91 = 11 kcal/mol: 3° radical forms more easily than $CH_3•$.

TRAPS

- ✕ **Using full-headed arrows for single-electron moves** Homolysis needs fish-hook (half) arrows.
- ✕ **Placing 3° radicals above benzyl and allyl** The book's own bond energies (3° 91, benzyl 88, allyl 86 kcal/mol) put benzyl and allyl first.

7 Carbocations: Structure and Stability



- Carbocation: sp^2, trigonal planar, six electrons, empty p orbital.
- Stabilised by alkyl groups (+I, hyperconjugation), adjacent lone pairs (full octets) and resonance; destabilised by −I groups.
- Reactivity runs opposite to stability.

STANDARD RESULTS

3° > 2° > 1° > CH_3^+ (9, 6, 3, 0 α-H).

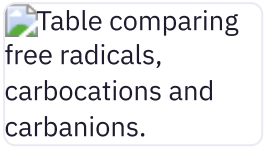
p-OCH_3 > p-CH_3 > H > p-NO_2 (benzyl cations).

TRAPS

- ✕ **Confusing reactivity with stability** The least stable cation (CH_3^+) is the most reactive.
- ✕ **Assuming the n-propyl cation is resonance-stabilised like allyl** It has no π bond next to C^+.
- ✕ **Calling the carbocation carbon sp³ or tetrahedral** It is sp² and trigonal planar, with an empty p orbital.

8 Carbanions: Structure and Stability

- Carbanion: 8 electrons, negative charge, nucleophile; sp³ pyramidal like NH_3, diamagnetic.
- Stabilised by –I groups, s-character and resonance; destabilised by +I groups.
- Radical (7 e, planar, paramagnetic) vs cation (6 e, planar) vs anion (8 e, pyramidal).


Table comparing free radicals, carbocations and carbanions.

STANDARD RESULTS

CH_3^- > 1° > 2° > 3°.

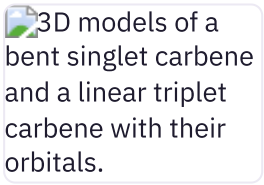
$HC{\equiv}C^-$ (sp) > $CH_2{=}CH^-$ (sp^2) > alkyl (sp^3).

TRAPS

- ✕ **Copying the carbocation order for carbanions** Alkyl groups destabilise carbanions, so 3° is the least stable.
- ✕ **Calling every carbanion sp³** When the charge is delocalised into C=O or a ring, the carbon becomes planar.

9 Carbenes: Singlet, Triplet and Their Reactions

- Carbene: neutral carbon with two bonds and two non-bonded electrons (6 e).
- Singlet (paired, bent, reactive) vs triplet (unpaired diradical, ground state); multiplicity 1 vs 3.
- Reactions: cyclopropanation, C–H insertion, ring expansion; carbylamine (1° amines only) and Reimer–Tiemann (:CCl_2 is the electrophile).


3D models of a bent singlet carbene and a linear triplet carbene with their orbitals.

STANDARD RESULTS

$CHCl_3$ + base → :CCl_2 (α-elimination).

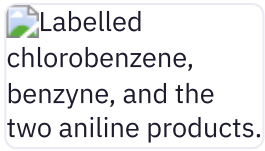
Butane + :CH_2 → pentane + 2-methylbutane.

TRAPS

- ✕ **Calling the singlet the ground (more stable) state of :CH_2** The triplet is more stable.
- ✕ **Saying secondary amines also give the carbylamine test** Only primary amines do: two H on N are lost as HCl.

10 Nitrenes and Benzyne

- Nitrene: neutral univalent N with a sextet; from azides; adds to C=C (aziridines), inserts into C–H.
- Benzyne: aromatic, with a weak extra bond from in-plane sp^2 overlap; formed from aryl halides and strong bases.
- Elimination–addition: the nucleophile can enter ortho to the leaving group's carbon (cine-substitution).


Labelled chlorobenzene, benzyne, and the two aniline products.

STANDARD RESULTS

^{14}C-chlorobenzene + NH_2^-: two anilines, ≈ 47 % and 53 %.

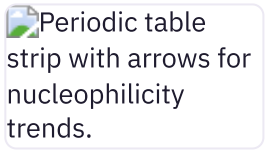
o-Chlorotoluene → 3-methylbenzyne → o- + m-toluidine.

TRAPS

- ✕ **Assuming the nucleophile always takes the leaving group's position** Via benzyne it can enter at the adjacent carbon (cine-substitution).
- ✕ **Treating benzyne as an ordinary alkyne** It stays aromatic; its third bond is a weak in-plane sp^2–sp^2 overlap.

11 Electrophiles, Nucleophiles and Ambident Reagents

- Electrophiles: electron-poor Lewis acids, positive or neutral; nucleophiles: electron-rich Lewis bases.
- Charged > neutral; across a period nucleophilicity follows basicity; down a group (protic solvent) it reverses.
- Ambident nucleophiles (CN^-, NO_2^-) attack through two atoms.


Periodic table strip with arrows for nucleophilicity trends.

STANDARD RESULTS

CH_3S^- > CH_3O^- > CH_3COO^- > H_2O.

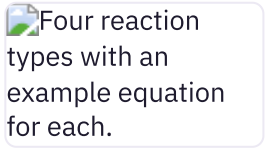
I^- > Br^- > Cl^- > F^- in methanol.

TRAPS

- ✕ **Assuming every electrophile is charged** BF_3, $AlCl_3$ and SO_3 are neutral electrophiles.
- ✕ **Assuming the stronger base is always the stronger nucleophile** Down a group in protic solvents the order reverses: I^- > F^-.

12 Types of Organic Reactions

- Substitution: one group replaces another; skeleton unchanged.
- Addition: π bonds become σ bonds; elimination is the reverse (β, α or γ).


Four reaction types with an example equation for each.

- Rearrangement: atoms move, formula kept (NH_4CNO → urea, Fries, Beckmann).

STANDARD RESULTS

1,3-Dibromopropane + Zn → cyclopropane (γ, Freund).

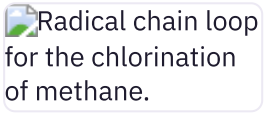
$CHCl_3$ + base → $:CCl_2$ (α).

TRAPS

✕ **Calling every reaction of an alkene an addition** Propene + Cl_2 at 500 °C substitutes at the allylic position.

✕ **Confusing α- and β-elimination** α: both groups leave the same carbon (carbene); β: adjacent carbons (alkene).

13 Free Radical Substitution: Chlorination of Methane and NBS


Radical chain loop for the chlorination of methane.

- Radical chains: initiation, propagation (radical in, radical out), termination; inhibitors stop them.
- Halogen reactivity $F_2 > Cl_2 > Br_2 > I_2$ is set by the H-abstraction step; iodination is endothermic.
- NBS keeps Br_2 low, so allylic/benzylic substitution wins over addition.

STANDARD RESULTS

Bromination: +18 + (−24) = −6 kcal/mol.

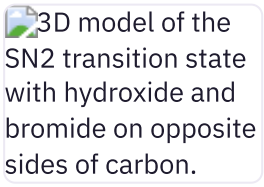
But-1-ene + NBS → 3-bromobut-1-ene (+ 1-bromobut-2-ene).

TRAPS

✕ **Judging reactivity from the overall ΔH alone** The slow, endothermic first propagation step controls the rate.

✕ **Writing Br_2 addition across C=C with NBS** NBS keeps Br_2 low, so allylic substitution wins.

14 SN2 Reaction: Mechanism, Walden Inversion and Rates


3D model of the SN2 transition state with hydroxide and bromide on opposite sides of carbon.

- SN2: one step, second order, backside attack through a five-coordinate transition state; complete (Walden) inversion.
- Steric hindrance controls the rate: CH_3 > 1° > 2° > 3°; β-bulk (neopentyl) also slows it; α-C=O, allyl and benzyl speed it.
- Strong nucleophile, weak-base leaving group, polar aprotic solvent.

STANDARD RESULTS

(R)-2-iodobutane + OH^- → (S)-butan-2-ol.

1° : 2° = 40 000 : 500 = 80.

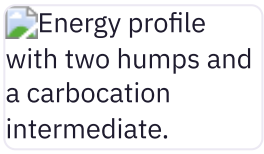
TRAPS

✕ **Assuming inversion always flips the R/S label** The label flips only when the incoming group takes the leaving group's priority rank.

✕ **Treating neopentyl bromide as a fast primary substrate** The bulky β-carbon makes it about as slow as a 3° halide.

✕ **Choosing a protic solvent for SN2 because it is polar** Hydrogen bonding cages the nucleophile; use a polar aprotic solvent.

15 SN1 Reaction: Carbocations, Racemisation and Rearrangement


Energy profile with two humps and a carbocation intermediate.

- SN1: two steps, first order (Rate = k[RX]); slow ionisation to a planar carbocation.
- Stereochemistry: racemisation with a slight excess of inversion.
- Carbocations may rearrange (1,2-H or CH_3 shift) before capture.

STANDARD RESULTS

Doubling $[OH^-]$: no change in SN1 rate.

3-Bromo-2,2-dimethylbutane + H_2O → 2,3-dimethylbutan-2-ol.

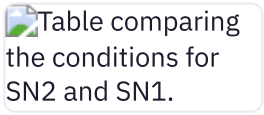
TRAPS

✕ **Writing 100 % racemisation for SN1** Some excess inversion is usual: the leaving ion shields the front face.

✕ **Putting [Nu] in the SN1 rate law** Rate = k[RX]; the nucleophile is not in the slow step.

✕ **Stopping at the first carbocation** Check whether a neighbouring H or CH_3 can shift to make a more stable cation.

16 SN1 vs SN2: Substrate, Leaving Group and Solvent


Table comparing the conditions for SN2 and SN1.

- SN1 rate follows carbocation stability; the leaving group matters more than in SN2.
- Polar, ionising solvents speed SN1 enormously (water ≫ ethanol).
- Choose by substrate, nucleophile and solvent together; 2° halides can go either way.

STANDARD RESULTS

$C_6H_5CH_2Br \approx (CH_3)_3CBr > (CH_3)_2CHBr > CH_3CH_2Br$ (SN1).

EtBr + NaCN/DMF: SN2; $(CH_3)_3CCl$/HCOOH: SN1.

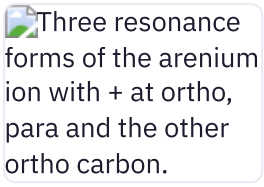
TRAPS

✕ **Assuming secondary halides always go by SN1** With a strong, concentrated nucleophile they follow SN2.

✕ **Ignoring the solvent** Polar protic solvents speed SN1 but slow SN2.

17 Electrophilic Substitution: SE1 and SE2 in Benzene

- SE1 is rare and aliphatic; SE2 is the benzene mechanism.
- Step 1 makes a strong electrophile with a Lewis acid or conc. H_2SO_4.
- Step 2 (slow) gives the resonance-stabilised arenium ion; step 3 (fast) loses H^+ and restores aromaticity.


Three resonance forms of the arenium ion with + at ortho, para and the other ortho carbon.

STANDARD RESULTS

$HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + 2HSO_4^- + H_3O^+$.

Benzene + $CH_3COCl/AlCl_3$ → acetophenone.

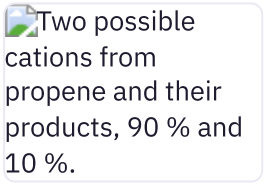
TRAPS

✕ **Making proton loss the slow step** Forming the arenium ion (losing aromaticity) is rate-determining.

✕ **Letting the arenium ion add a nucleophile** It loses H^+ instead, to restore aromaticity: substitution, not addition.

18 Electrophilic Addition: Markovnikov's Rule and Rearrangements

- Two steps: electrophile adds (slow, carbocation), nucleophile captures (fast).
- Markovnikov's rule follows from carbocation stability.
- Carbocations may rearrange by 1,2-H, CH_3 or Ph shifts before capture.


Two possible cations from propene and their products, 90 % and 10 %.

STANDARD RESULTS

Propene + HBr → 2-bromopropane (90 %).

3-Methylpent-1-ene + HBr → 3-bromo-3-methylpentane.

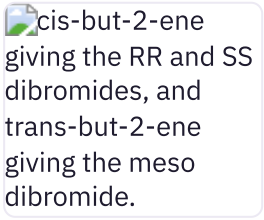
TRAPS

✕ **Learning the rule as 'H goes to the carbon with more H' without the reason** It fails for alkenes with −I/−M groups (see the peroxide-effect part); the rule is really 'form the more stable carbocation'.

✕ **Stopping at the first carbocation** Check whether a neighbouring H, CH_3 or Ph can shift to make it 3°.

19 Anti-Addition of Bromine and 1,4-Addition to Dienes

- Br_2 adds through a cyclic bromonium ion: anti-addition, stereoselective.
- Conjugated dienes add 1,2 and 1,4 through an allylic cation.


cis-but-2-ene giving the RR and SS dibromides, and trans-but-2-ene giving the meso dibromide.

STANDARD RESULTS

cis-But-2-ene + Br_2 → racemic; trans → meso-2,3-dibromobutane.

Buta-1,3-diene + HBr: low T → 3-bromobut-1-ene; high T → 1-bromobut-2-ene.

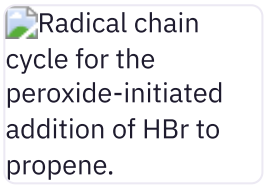
TRAPS

✕ **Swapping meso and racemic** For a symmetric alkene with anti-addition: cis gives racemic (RR + SS), trans gives meso.

✕ **Giving only the 1,2-product for a conjugated diene** The allylic cation carries + on C-2 and C-4, so the 1,4-product forms too, and wins at high temperature.

20 Peroxide Effect: Anti-Markovnikov Addition

- Peroxide effect: HBr adds anti-Markovnikov by a radical chain; Br• adds first.
- Only HBr: both propagation steps exothermic.
- −I/−M groups on C=C and radical halogen additions also give anti-Markovnikov products.


Radical chain cycle for the peroxide-initiated addition of HBr to propene.

STANDARD RESULTS

Propene + HBr (peroxide) → 1-bromopropane.

Acrolein + HCl → 3-chloropropanal; acrylonitrile + HBr → $BrCH_2CH_2CN$.

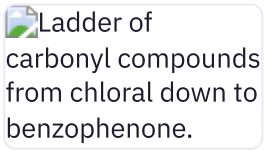
TRAPS

✕ **Applying the peroxide effect to HCl or HI** Only HBr has both propagation steps exothermic; HCl and HI still add by Markovnikov's rule with peroxide.

✕ **Thinking peroxide makes H add to the more substituted carbon** Br• adds first, to the end that gives the more stable radical; H comes last, from HBr.

21 Nucleophilic Addition to the Carbonyl Group

- Nucleophile attacks the carbonyl carbon in the slow step; H^+ then adds to O.
- For HCN the attacker is CN^-: base catalyses, acid retards.
- +I alkyl groups and bulk lower reactivity: aldehydes > ketones.


Ladder of carbonyl compounds from chloral down to benzophenone.

STANDARD RESULTS

Acetone + HCN → acetone cyanohydrin.

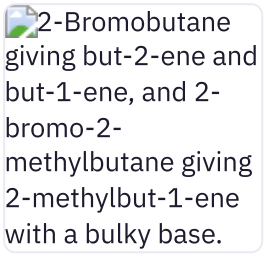
HCHO > CH_3CHO > CH_3COCH_3; CH_3CHO + CH_3MgBr, then H_2O → propan-2-ol.

TRAPS

✕ **Giving only one reason why ketones are less reactive** There are two: the +I effect of the alkyl groups (lower δ+) and their bulk (steric hindrance).

✕ **Taking HCN itself as the attacking species** The nucleophile is CN^-; that is why bases speed the reaction and acids slow it.

22 E1 and E1cB Eliminations: Saytzeff vs Hofmann



- E1: carbocation first; competes with SN1; 3° > 2° > 1°.
- Saytzeff: more substituted alkene; bulky base → Hofmann alkene.
- Alcohols dehydrate with acid by E1 (1° by E2); E1cB: carbanion first.

STANDARD RESULTS

2-Bromobutane + $C_2H_5O^-$ → but-2-ene (81 %) + but-1-ene (19 %).

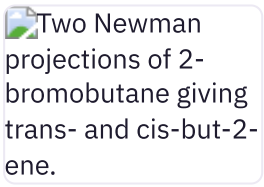
Pentan-2-ol (H_2SO_4) → pent-2-ene (80 %); CF_3CHCl_2 + EtO^- → $CF_2{=}CCl_2$.

TRAPS

✕ **Applying Saytzeff with every base** A bulky base such as KO-t-Bu gives mainly the Hofmann (less substituted) alkene.

✕ **Forgetting that E1 carbocations can rearrange** As in SN1, a 1,2-H or CH_3 shift can occur before H^+ is lost.

23 E2 Elimination and Anti-periplanar Geometry



- E2 is concerted and bimolecular: Rate = k[RX][Base].
- C–X breaks in the slow step, so better leaving groups react faster.
- H and X must be anti-periplanar, so E2 is stereospecific.

STANDARD RESULTS

$PhCH_2CH_2Br$ reacts 600 × faster than $PhCH_2CH_2Cl$.

2-Bromobutane (H anti to Br, methyls anti) → trans-but-2-ene.

TRAPS

✕ **Removing any β-H in E2** Only a β-H anti-periplanar to the leaving group can be removed.

✕ **Expecting rearrangement in E2** E2 is one step with no carbocation; a rearranged alkene points to E1.

Mechanism of Organic Reactions

−I order $NR_3^+ > NO_2 > SO_2R > CN > COOH > F > Cl > Br > I > OR > COR > OH > C_6H_5 > CH{=}CH_2 > H$ **+I order** $(CH_3)_3C > (CH_3)_2CH > CH_3CH_2 > CH_3 > D > H$

Intermediates carbocations, radicals: 3° > 2° > 1° > CH_3 · carbanions: CH_3 > 1° > 2° > 3° **Leaving groups** $I^- > Br^- > Cl^- > F^-$

1 Inductive Effect: −I and +I Groups

$\mu(CH_3I)$ = 1.64 D, $\mu(CH_3Br)$ = 1.79 D, $\mu(CH_3Cl)$ = 1.83 D

- −I: $NO_2 > CN > COOH > F > Cl > Br > I > OH > H$; +I: t-Bu > i-Pr > Et > Me > H. Fades after C_2.

2 Acid Strength: pKa and Carboxylic Acids

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$$pK_a = -\log K_a$$

$$K_b = \frac{[B^+][OH^-]}{[BOH]}$$

$$pK_b = -\log K_b$$

- Lower pK_a = stronger acid. −I (more, nearer halogens) strengthens; +I weakens; HCOOH > CH_3COOH.

3 Acidity of Alcohols and Hydrocarbons, Basicity of Amines

pK_b: $(CH_3)_2NH$ 3.23 < CH_3NH_2 3.32 < $(CH_3)_3N$ 4.2

- Phenol > H_2O > 1° > 2° > 3° ROH; HC≡CH > $CH_2{=}CH_2$ > C_2H_6. Methylamines (aq): 2° > 1° > 3° > NH_3.

4 Electromeric and Mesomeric (Resonance) Effects

- Electromeric: temporary, on demand. +M: OH, OR, NH_2, X; −M: NO_2, CN, CHO, COOH. M beats I.

5 Hyperconjugation and the Baker–Nathan Effect

>C=C< + $H_2 \longrightarrow$ >CH−CH< + *E* (heat of hydrogenation)

C–C : 1.54 Å (propane) → 1.46 Å (propene)

μ: HCHO 2.27 D, CH_3CHO 2.72 D

- No-bond forms = number of α-H: more α-H, more stable alkene, cation, radical (3° > 2° > 1°).

6 Bond Fission and Free Radicals

- Homolysis → radicals (hv, heat, peroxide); heterolysis → ions. Radicals: allyl ≈ benzyl > 3° > 2° > 1° > $CH_3^{\cdot}$.

7 Carbocations: Structure and Stability

- R^+: 6 e, sp^2, planar. Benzyl ≈ allyl ≈ 3° > 2° > 1° > CH_3^+.

8 Carbanions: Structure and Stability

- R^-: 8 e, sp^3 pyramidal. CH_3^- > 1° > 2° > 3°; −I, C=O, CN, NO_2 stabilise.

9 Carbenes: Singlet, Triplet and Their Reactions

$$\text{Spin multiplicity} = 2\sum s + 1$$

singlet: $2\left(\frac{1}{2} - \frac{1}{2}\right) + 1 = 1$

triplet: $2\left(\frac{1}{2} + \frac{1}{2}\right) + 1 = 3$

- Carbene: 6 e. Singlet (bent, stereospecific addition) vs triplet (diradical, more stable); $CHCl_3$ + base → $:CCl_2$.

10 Nitrenes and Benzyne

- Nitrene R–N: from RN_3, + C=C → aziridine. Benzyne: ArX + $NaNH_2$ → cine-substitution.

11 Electrophiles, Nucleophiles and Ambident Reagents

- E^+ = Lewis acid, Nu = Lewis base. Protic: $I^- > Br^- > Cl^- > F^-$; ambident: CN^-, NO_2^-.

12 Types of Organic Reactions

- Substitution, addition, elimination (α → carbene, β → alkene), rearrangement.

13 Free Radical Substitution: Chlorination of Methane and NBS

$$\Delta H_{overall} = \Delta H_{step\ 1} + \Delta H_{step\ 2}$$

- Chain: initiation, 2 propagation steps, termination; F > Cl > Br > I. NBS: allylic bromination.

14 SN2 Reaction: Mechanism, Walden Inversion and Rates

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

- S_N2: one step, inversion; CH_3 > 1° > 2° > 3°; strong Nu, polar aprotic solvent.

15 SN1 Reaction: Carbocations, Racemisation and Rearrangement

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

- S_N1: R^+ (slow), racemisation, possible 1,2-shifts.

16 SN1 vs SN2: Substrate, Leaving Group and Solvent

- S_N1: 3°, weak Nu, polar protic. S_N2: CH_3/1°, strong Nu, aprotic.

17 Electrophilic Substitution: SE1 and SE2 in Benzene

- S_E2 (benzene): E^+ → arenium ion (slow) → $-H^+$ (fast).

18 Electrophilic Addition: Markovnikov's Rule and Rearrangements

- E^+ (slow) then Nu^-; Markovnikov = more stable cation; check 1,2-shifts.

19 Anti-Addition of Bromine and 1,4-Addition to Dienes

- Br_2 anti (bromonium): cis → racemic, trans → meso. Dienes: 1,2 (low T), 1,4 (high T).

20 Peroxide Effect: Anti-Markovnikov Addition

- HBr + peroxide: $Br^{\cdot}$ first → anti-Markovnikov. Only HBr.

21 Nucleophilic Addition to the Carbonyl Group

- Nu^- attacks C=O (slow); HCHO > CH_3CHO > CH_3COCH_3.

22 E1 and E1cB Eliminations: Saytzeff vs Hofmann

- E1: R^+ first; E1cB: carbanion first. Saytzeff; bulky base → Hofmann.

23 E2 Elimination and Anti-periplanar Geometry

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

- E2: one step, H and X anti-periplanar; 2-bromobutane → trans-but-2-ene.