ANSWER KEY

Organic Chemistry 1: Practice Exam

Quick answers first, then a worked solution for every problem.

#	Topic	Answer
1	Functional groups	Carboxylic acid, ester, aromatic ring
2	IUPAC naming	4-ethyl-2-methylhexane
3	Resonance	Two equivalent structures; each C–O bond is about 1.5 bonds
4	Acidity and pKa	(a) Acetic acid > phenol > ethanol (b) Right
5	Conformations of butane	Anti > gauche > eclipsed (CH_3/H) > eclipsed (CH_3/CH_3)
6	Chair conformations	The methyl
7	R/S configuration	R (D-glyceraldehyde)
8	Stereoisomers	3 (one pair of enantiomers plus a meso compound)
9	SN1, SN2, E1 or E2	(a) SN2 (b) SN1 (+ some E1) (c) E2, trans-2-butene (d) E2, 2-methylpropene
10	SN2 stereochemistry and rate	(a) (S)-2-iodobutane (b) The rate doubles
11	Carbocation rearrangement	2-bromo-2-methylbutane
12	Alkene additions	(a) 1-bromo-1-methylcyclohexane (b) 1-bromo-2-methylcyclohexane (c) trans-2-methylcyclohexan-1-ol (d) 1-methylcyclohexan-1-ol
13	Halogen additions	(a) trans-1,2-dibromocyclohexane (b) trans-2-bromocyclohexan-1-ol
14	Alkyne reactions	(a) cis-2-butene (b) trans-2-butene (c) 2-butanone (d) butanal

15	Multistep synthesis	Br_2/light → $KOC(CH_3)_3$, heat → BH_3·THF then H_2O_2, NaOH

1. Functional groups

Name every functional group in aspirin, 2-acetoxybenzoic acid ($CH_3COO–C_6H_4–COOH$).

1. –COOH: **carboxylic acid**.
2. $CH_3C(=O)O–$ attached to the ring through oxygen: **ester**.
3. C_6H_4: **aromatic ring** (benzene).

> **How to explain it:** Look at what the C=O is attached to. C=O next to OH is an acid, C=O next to O–C is an ester, C=O between two carbons is a ketone. Calling the ester a ketone or an ether is the usual mistake.

2. IUPAC naming

Name $CH_3CH(CH_3)CH_2CH(CH_2CH_3)CH_2CH_3$.

1. Longest chain: 6 carbons, so the parent is hexane.
2. Numbering from the left puts substituents at 2 and 4; from the right, at 3 and 5. Use the lower set: 2, 4.
3. Methyl on C2, ethyl on C4. List alphabetically: **4-ethyl-2-methylhexane**.

> **How to explain it:** Draw it out and trace every possible chain, since branches can hide carbons. Number for the lowest first point of difference, then alphabetize, ignoring prefixes like di- and tri-.

3. Resonance

Draw the resonance structures of the acetate ion, CH_3COO^-. Why are both C–O bonds the same length?

1. Structure A: C=O on the top oxygen, negative charge on the bottom oxygen.
2. Push a lone pair from O^- down into a new C=O bond, and push the old C=O π electrons up onto the other oxygen. Structure B is the mirror image.
3. The real ion is a blend: each C–O bond is about 1.5 bonds, and each oxygen carries half the negative charge.

> **How to explain it:** Curved arrows move electrons, never atoms, and never break single bonds. Arrows start at a lone pair or a π bond and end where the electrons go.

4. Acidity and pKa

(a) Rank by acidity: ethanol (pKa 16), acetic acid (pKa 4.8), phenol (pKa 10). (b) Which side does $CH_3COOH + CH_3CH_2O^- \rightleftharpoons CH_3COO^- + CH_3CH_2OH$ favor?

1. (a) **Acetic acid > phenol > ethanol.** Acetate spreads its charge over two oxygens, phenoxide spreads it into the ring (onto carbons), and ethoxide can't spread it at all.
2. (b) Equilibrium favors the weaker acid. Ethanol (pKa 16) is far weaker than acetic acid (4.8), so it lies **to the right**, by about 10^{11}.

> **How to explain it:** Judge an acid by its conjugate base: the more stable the base, the stronger the acid. Use ARIO (atom, resonance, induction, orbital) in that order.

5. Conformations of butane

Looking down the C2–C3 bond of butane, rank these conformations from most to least stable: anti, gauche, eclipsed with CH_3 over H, and eclipsed with CH_3 over CH_3.

1. **Anti** (methyls 180° apart) is the most stable.
2. **Gauche** (methyls 60° apart) is about 3.8 kJ/mol higher.
3. **Eclipsed, CH_3 over H** is higher still.
4. **Eclipsed, CH_3 over CH_3** is the least stable, about 19 kJ/mol above anti.

> **How to explain it:** Staggered beats eclipsed (torsional strain), and big groups want to be far apart (steric strain). Draw the Newman projection and rotate the back carbon 60° at a time.

6. Chair conformations

In the most stable chair of cis-1-tert-butyl-4-methylcyclohexane, which group is axial?

1. On a 1,4-disubstituted ring, cis means one group is axial and one is equatorial.
2. tert-Butyl is huge and suffers severe 1,3-diaxial strain when axial, so it takes the equatorial spot.
3. That leaves the **methyl axial**.

> **How to explain it:** Decide cis or trans first (up/up or up/down), then let the biggest group go equatorial. Putting both groups equatorial would make it the trans isomer.

7. R/S configuration

In a Fischer projection of glyceraldehyde, CHO is on top, CH_2OH is on the bottom, OH is on the right and H is on the left. Is this R or S?

1. Priorities: OH (1) > CHO (2) > CH_2OH (3) > H (4).
2. Trace 1 → 2 → 3: right → top → bottom goes counterclockwise, which reads as S.
3. H is on a horizontal line (pointing toward you), so reverse it: **R** (this is D-glyceraldehyde).

> **How to explain it:** Priority goes by atomic number at the first point of difference. If the lowest priority points toward you, reverse your answer. Forgetting that flip is the most common R/S error.

8. Stereoisomers

How many stereoisomers does 2,3-dibromobutane have, and how are they related?

1. Two stereocenters allow up to $2^2 = 4$.
2. (2R,3R) and (2S,3S) are **enantiomers**.
3. (2R,3S) and (2S,3R) are the same molecule: it has an internal mirror plane, so it's **meso** and achiral.
4. Total: **3 stereoisomers**. The meso form is a diastereomer of each enantiomer.

> **How to explain it:** 2^n is a maximum, not a guarantee. When both stereocenters carry the same groups, check for a mirror plane.

9. SN1, SN2, E1 or E2

Give the main mechanism and product: (a) 1-bromobutane + NaCN in DMSO; (b) 2-bromo-2-methylpropane in methanol, no added base; (c) 2-bromobutane + $NaOCH_2CH_3$ in ethanol, heat; (d) 2-bromo-2-methylpropane + $KOC(CH_3)_3$.

1. (a) Primary + good nucleophile + polar aprotic solvent: **SN2** → pentanenitrile, $CH_3CH_2CH_2CH_2CN$.
2. (b) Tertiary + weak nucleophile + protic solvent: **SN1** → 2-methoxy-2-methylpropane, with some 2-methylpropene from E1.
3. (c) Secondary + strong base + heat: **E2** → mostly trans-2-butene (Zaitsev product).
4. (d) Tertiary + bulky strong base: **E2** → 2-methylpropene.

> **How to explain it:** Ask three questions in order: what's the substrate (1°, 2°, 3°)? Strong or weak nucleophile or base? Protic or aprotic solvent? Tertiary never does SN2, and primary almost never does SN1.

10. SN2 stereochemistry and rate

(R)-2-Bromobutane reacts with NaI in acetone. (a) What is the product? (b) What happens to the rate if $[I^-]$ doubles?

1. (a) SN2 attacks from the back side and inverts the stereocenter: **(S)-2-iodobutane**.
2. (b) Rate = k[RBr][I^-], so the rate **doubles**.

> **How to explain it:** Show the umbrella flipping inside out. Inversion here also changes R to S because I takes Br's place as the top priority; that doesn't always happen, so check the priorities.

11. Carbocation rearrangement

What is the major product of 3-methyl-2-butanol with HBr?

1. H^+ protonates the OH, and water leaves, giving a secondary carbocation on C2.
2. A hydride shifts from C3 to C2, making a more stable tertiary carbocation on C3.
3. Br^- adds to the tertiary carbon: **2-bromo-2-methylbutane**.

> **How to explain it:** Any time a carbocation forms, check its neighbors for a shift that makes it more stable. Students who skip this answer 2-bromo-3-methylbutane.

12. Alkene additions

Give the product of 1-methylcyclohexene with (a) HBr; (b) HBr and peroxides; (c) BH_3·THF, then H_2O_2, NaOH; (d) H_2O, H_2SO_4.

1. (a) Markovnikov, through the tertiary carbocation: **1-bromo-1-methylcyclohexane**.
2. (b) Radical addition, anti-Markovnikov: **1-bromo-2-methylcyclohexane** (cis and trans).
3. (c) Anti-Markovnikov and syn: **trans-2-methylcyclohexan-1-ol** (H and OH add to the same face, so OH ends up trans to CH_3).
4. (d) Markovnikov hydration: **1-methylcyclohexan-1-ol**.

> **How to explain it:** Make a reagent chart with two columns: where the group goes (Markovnikov or anti) and which face (syn, anti or either). Hydroboration is the one that's anti-Markovnikov and syn.

13. Halogen additions

What forms when cyclohexene reacts with (a) Br_2 in CH_2Cl_2 and (b) Br_2 in water?

1. (a) Br_2 forms a bromonium ion, and Br^- opens it from the back: **trans-1,2-dibromocyclohexane** (anti addition, racemic).
2. (b) Water outnumbers Br^- and opens the bromonium instead: **trans-2-bromocyclohexan-1-ol** (a bromohydrin).

> **How to explain it:** The bromonium blocks one face, so the second group has to come in from the other side. Drawing the cis product is the giveaway that a student skipped the bromonium.

14. Alkyne reactions

Give the products: (a) 2-butyne + H_2, Lindlar catalyst; (b) 2-butyne + Na, NH_3(l); (c) 1-butyne + H_2O, H_2SO_4, $HgSO_4$; (d) 1-butyne + 9-BBN, then H_2O_2, NaOH.

1. (a) Syn addition of H_2, stopping at the alkene: **cis-2-butene**.
2. (b) Dissolving-metal reduction: **trans-2-butene**.
3. (c) Markovnikov hydration gives an enol that tautomerizes: **2-butanone**.
4. (d) Anti-Markovnikov hydration, then tautomerization: **butanal**.

> **How to explain it:** Lindlar gives cis, sodium in ammonia gives trans. Hydrating an alkyne never stops at the enol; it always ends as a carbonyl.

15. Multistep synthesis

Show how to make 2-methyl-1-propanol, $(CH_3)_2CHCH_2OH$, from 2-methylpropane.

1. Br_2, light: bromination picks the tertiary hydrogen, giving 2-bromo-2-methylpropane.
2. $KOC(CH_3)_3$, heat: E2 gives 2-methylpropene.
3. BH_3·THF, then H_2O_2, NaOH: anti-Markovnikov hydration puts OH on the end carbon, giving **2-methyl-1-propanol**.

> **How to explain it:** Work backward. A primary OH next to a branch points to hydroboration of an alkene, the alkene comes from an elimination, and the halide comes from radical bromination. There's no one-step way to put OH on an alkane.