ANSWER KEY

Organic Chemistry 2: Practice Exam

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

#	Topic	Answer
1	IR spectroscopy	(a) Acetone (b) Propanal (c) Allyl alcohol
2	^{1}H NMR	Ethyl acetate
3	Degrees of unsaturation	Ethylbenzene
4	Mass spectrometry with NMR	2-Bromopropane
5	Conjugated dienes: kinetic vs thermodynamic	−80 °C: 3-bromo-1-butene; 40 °C: 1-bromo-2-butene
6	Diels–Alder	cis-4-Cyclohexene-1,2-dicarboxylic anhydride
7	Aromaticity	Aromatic: benzene, cyclopentadienyl anion, tropylium, pyridine. Antiaromatic: cyclobutadiene. Nonaromatic: cyclooctatetraene
8	Electrophilic aromatic substitution: directing effects	(a) Anisole > toluene > benzene > chlorobenzene > nitrobenzene (b) Anisole ortho/para; nitrobenzene meta
9	Synthesis order on a benzene ring	(a) Nitrate first, then brominate (b) Brominate first, then nitrate
10	Oxidizing alcohols	(a) Butanal (b) Butanoic acid (c) 2-Butanone (d) No reaction
11	Opening epoxides	(a) 1-Methoxy-2-methyl-2-propanol (b) 2-Methoxy-2-methyl-1-propanol
12	Grignard synthesis	PhMgBr + 2-butanone; CH_3MgBr + propiophenone; CH_3CH_2MgBr + acetophenone (each then H_3O^+)
13	Carboxylic acid derivatives	(a) Acid chloride > anhydride > ester > amide (b) Methyl acetate; acetamide; no reaction

14	Aldol reaction	3-Hydroxy-2-methylpentanal; then 2-methylpent-2-enal
15	Acetoacetic ester synthesis	NaOEt → CH_3CH_2Br → H_3O^+, heat

1. IR spectroscopy

Three isomers of C_3H_6O give these IR spectra. Identify each. (a) Strong peak at 1715 cm^{-1}, nothing at 2720 or 3300. (b) Strong peak at 1730 cm^{-1} plus two weak peaks near 2720 and 2820 cm^{-1}. (c) Broad peak at 3300 cm^{-1} and a peak at 1645 cm^{-1}, no peak near 1700.

1. (a) C=O with no aldehyde C–H: a ketone, **acetone** (propanone).
2. (b) C=O plus the aldehyde C–H pair: **propanal**.
3. (c) O–H and C=C but no C=O: **allyl alcohol** (prop-2-en-1-ol).

> **How to explain it:** Check four regions first: broad 3300 (O–H), sharp 1700ish (C=O), 2720 (aldehyde C–H), 1650 (C=C). Most exam IR questions are settled by these alone.

2. ^{1}H NMR

$C_4H_8O_2$ shows δ 1.26 (triplet, 3H), 2.05 (singlet, 3H), 4.12 (quartet, 2H). Identify it.

1. Triplet 3H plus quartet 2H: an ethyl group (CH_3CH_2–).
2. The CH_2 sits at 4.12 ppm, so it's bonded to oxygen.
3. The 3H singlet at 2.05 is a CH_3 next to C=O with no neighbors.
4. Put together: **ethyl acetate**, $CH_3COOCH_2CH_3$.

> **How to explain it:** Use the n + 1 rule for splitting and the shift for neighbors. Methyl propanoate has the same formula, but its OCH_3 singlet would sit near 3.7 ppm and its quartet near 2.3.

3. Degrees of unsaturation

C_8H_{10} shows ^{1}H NMR peaks at δ 7.1–7.3 (multiplet, 5H), 2.63 (quartet, 2H) and 1.23 (triplet, 3H). Identify it.

1. Degrees of unsaturation = (2C + 2 − H) / 2 = (16 + 2 − 10) / 2 = 4: one benzene ring (one ring + three C=C).
2. 5 aromatic H: a monosubstituted ring.
3. Quartet 2H plus triplet 3H: an ethyl group.
4. **Ethylbenzene**, $C_6H_5CH_2CH_3$.

> **How to explain it:** Four degrees of unsaturation is a benzene ring almost every time. The xylenes share the formula, but they'd show 4 aromatic H and a 6H singlet.

4. Mass spectrometry with NMR

A compound has molecular ion peaks at m/z 122 and 124 in a 1:1 ratio. Its ^{1}H NMR shows δ 1.71 (doublet, 6H) and 4.21 (septet, 1H). Identify it.

1. M and M + 2 in a 1:1 ratio means one bromine (^{79}Br and ^{81}Br are about equally common).
2. 122 − 79 = 43, which fits C_3H_7.
3. A 6H doublet plus a 1H septet is an isopropyl group, and the CH at 4.21 is on the Br carbon.
4. **2-Bromopropane**, $(CH_3)_2CHBr$.

> **How to explain it:** M + 2 peaks are fingerprints: 1:1 is bromine, 3:1 is chlorine. A doublet next to a septet always means isopropyl.

5. Conjugated dienes: kinetic vs thermodynamic

1,3-Butadiene reacts with HBr. What is the major product at -80 °C, and at 40 °C?

1. H^+ adds to C1, giving an allylic cation with + spread over C2 and C4.
2. At -80 °C, Br^- grabs the closest carbon, C2: **3-bromo-1-butene** (1,2-addition, kinetic product).
3. At 40 °C, the reaction can reverse and settles on the more stable, more substituted alkene: **1-bromo-2-butene** (1,4-addition, thermodynamic product).

> **How to explain it:** Cold = kinetic = forms fastest. Warm = thermodynamic = most stable product. Draw both resonance forms of the allylic cation first; each product comes from one of them.

6. Diels–Alder

What forms when 1,3-butadiene reacts with maleic anhydride (a cis dienophile)?

1. The diene (in its s-cis form) and the dienophile join in one step, forming two new σ bonds and a new six-membered ring with one C=C.
2. The two carbonyl groups were cis on the dienophile, so they stay cis on the ring.
3. Product: **cis-4-cyclohexene-1,2-dicarboxylic anhydride**.

> **How to explain it:** Count to six: 4 carbons from the diene plus 2 from the dienophile. Whatever is cis on the dienophile stays cis in the product, because it's one concerted step.

7. Aromaticity

Classify each as aromatic, antiaromatic or nonaromatic: benzene, cyclobutadiene, cyclooctatetraene, cyclopentadienyl anion, cycloheptatrienyl (tropylium) cation, pyridine.

1. **Aromatic:** benzene (6 π), cyclopentadienyl anion (6 π), tropylium cation (6 π), pyridine (6 π; the N lone pair isn't part of the ring's π system).
2. **Antiaromatic:** cyclobutadiene (4 π, planar).
3. **Nonaromatic:** cyclooctatetraene, which bends into a tub shape to avoid having 8 π electrons in a plane.

> **How to explain it:** Run the checklist: cyclic, planar, fully conjugated, 4n + 2 π electrons. Fail any of the first three and it's nonaromatic; pass them with 4n and it's antiaromatic.

8. Electrophilic aromatic substitution: directing effects

(a) Rank by rate of nitration: benzene, toluene, nitrobenzene, anisole, chlorobenzene. (b) Where does the nitro group go on anisole and on nitrobenzene?

1. (a) **Anisole > toluene > benzene > chlorobenzene > nitrobenzene.** OCH_3 donates strongly by resonance, CH_3 donates weakly, Cl withdraws, and NO_2 withdraws strongly.
2. (b) Anisole: **ortho/para** (mostly para). Nitrobenzene: **meta**.

> **How to explain it:** Activators push to ortho/para. Most deactivators push to meta. Halogens are the exception: they deactivate the ring but still direct ortho/para.

9. Synthesis order on a benzene ring

From benzene, make (a) m-bromonitrobenzene and (b) p-bromonitrobenzene.

1. (a) **Nitrate first** (HNO_3, H_2SO_4), then brominate (Br_2, $FeBr_3$). NO_2 directs Br to meta.
2. (b) **Brominate first** (Br_2, $FeBr_3$), then nitrate (HNO_3, H_2SO_4). Br directs to ortho and para; separate out the para product.

> **How to explain it:** The group that's already on the ring decides where the next one goes. Ask which group needs to be in charge, and put that one on first.

10. Oxidizing alcohols

Give the products: (a) 1-butanol + PCC; (b) 1-butanol + $Na_2Cr_2O_7$, H_2SO_4; (c) 2-butanol + PCC; (d) 2-methyl-2-propanol + $Na_2Cr_2O_7$, H_2SO_4.

1. (a) PCC stops a primary alcohol at the aldehyde: **butanal**.
2. (b) Chromic acid goes all the way: **butanoic acid**.
3. (c) Secondary alcohol to ketone: **2-butanone**.
4. (d) Tertiary alcohol, no H on the carbinol carbon: **no reaction**.

> **How to explain it:** Oxidation needs an H on the carbon holding the OH. Count those H's: two (primary), one (secondary), none (tertiary).

11. Opening epoxides

2,2-Dimethyloxirane is opened (a) with $NaOCH_3$ in CH_3OH and (b) with CH_3OH and a little H_2SO_4. Give each product.

1. (a) Basic, SN2-like: methoxide hits the **less hindered** CH_2 → **1-methoxy-2-methyl-2-propanol**.
2. (b) Acidic: the protonated epoxide opens at the **more substituted** carbon, which holds more positive charge → **2-methoxy-2-methyl-1-propanol**.

> **How to explain it:** Base attacks the less crowded side. Acid attacks the side that can best hold a positive charge. Same starting material, opposite products.

12. Grignard synthesis

Give three Grignard routes to 2-phenyl-2-butanol, $C_6H_5C(OH)(CH_3)CH_2CH_3$.

1. C_6H_5MgBr + 2-butanone, then H_3O^+.
2. CH_3MgBr + 1-phenyl-1-propanone (propiophenone), then H_3O^+.
3. CH_3CH_2MgBr + acetophenone, then H_3O^+.

> **How to explain it:** A tertiary alcohol has three groups on the carbinol carbon. Bring any one in as the Grignard and the other two come from the ketone. The acid workup is a separate step, because acid or any O–H or N–H destroys a Grignard.

13. Carboxylic acid derivatives

(a) Rank by reactivity: amide, acid chloride, ester, anhydride. (b) Predict: acetyl chloride + methanol; methyl acetate + NH_3; acetamide + methanol.

1. (a) **Acid chloride > anhydride > ester > amide.**
2. (b) Acetyl chloride + methanol → **methyl acetate** + HCl.
3. Methyl acetate + NH_3 → **acetamide** + methanol.
4. Acetamide + methanol → **no reaction**.

> **How to explain it:** Derivatives only go downhill, from more reactive to less reactive. The better the leaving group (Cl^- best, NH_2^- worst), the more reactive the derivative.

14. Aldol reaction

Propanal is treated with dilute NaOH. Give the aldol product, then the product after heating.

1. NaOH removes an α-H from C2, forming an enolate.
2. The enolate attacks the C=O of a second propanal: **3-hydroxy-2-methylpentanal**.
3. Heating removes water and forms a C=C conjugated with the C=O: **2-methylpent-2-enal**.

> **How to explain it:** The new C–C bond always joins the α-carbon of one molecule to the carbonyl carbon of the other. Number from the CHO to name it, and the methyl lands on C2.

15. Acetoacetic ester synthesis

Show how to make 2-pentanone from ethyl acetoacetate.

1. NaOEt in ethanol removes the acidic H between the two carbonyls (pKa about 11).
2. CH_3CH_2Br alkylates that carbon by SN2.
3. H_3O^+ and heat hydrolyze the ester and drive off CO_2: **$CH_3COCH_2CH_2CH_3$ (2-pentanone)**.

> **How to explain it:** The product is always a methyl ketone, $CH_3CO–CH_2–R$, where R comes from the alkyl halide. Work backward: find R, and that's your halide.