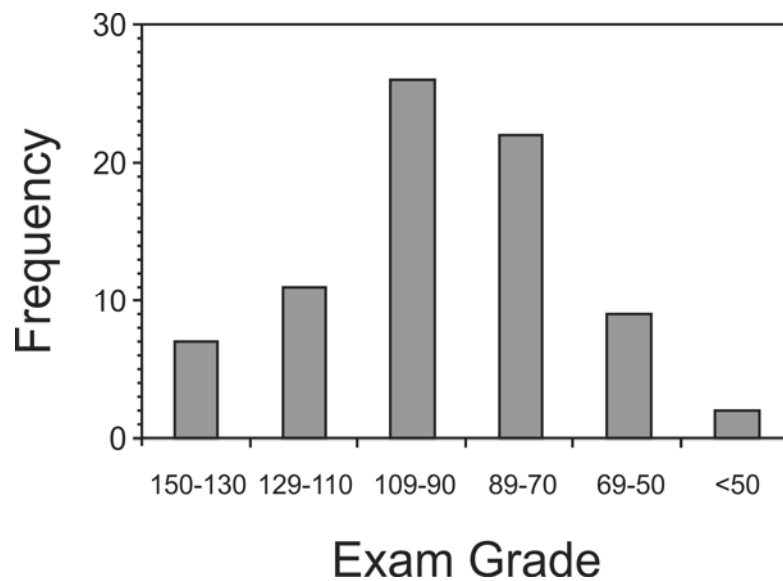
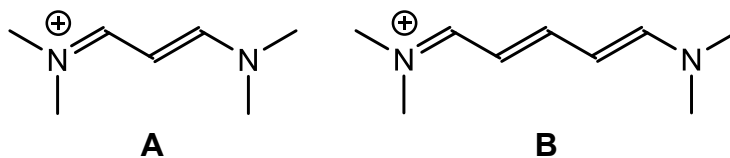


**Final Exam
Answer Key**

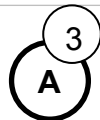
Final Exam Mean: 95
Final Exam Median: 93
Final Exam St. Dev.: 23



1. (9 pts) How do the two cyanine dyes **A** and **B** compare? For each question below, circle one answer.



Which will have a larger HOMO-LUMO gap?



A and B
will be the same

cannot determine

Which will absorb at longer wavelengths?



A and B
will be the same

cannot determine

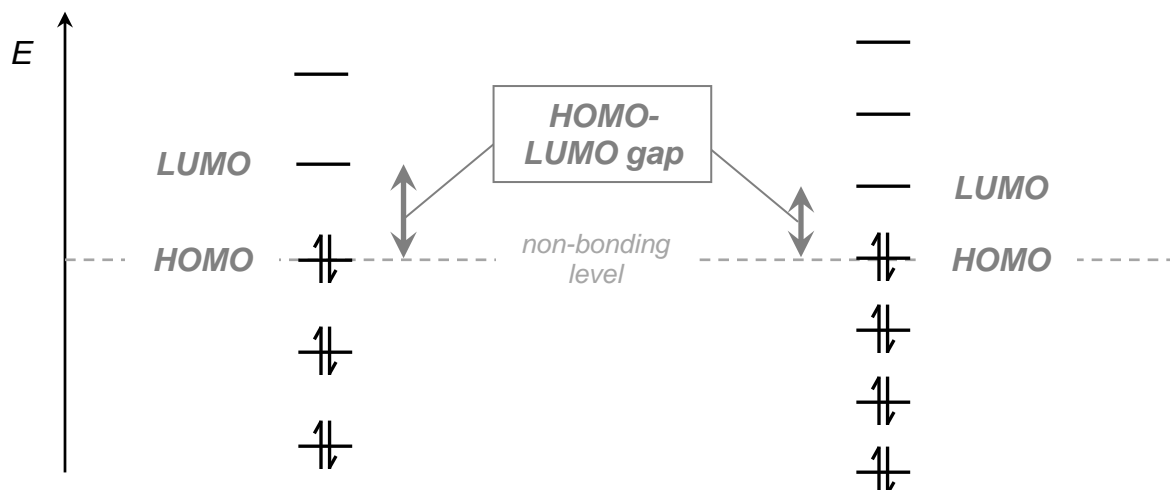
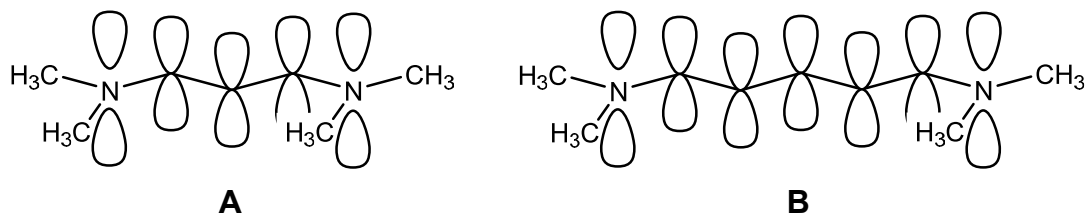
Which has more molecular orbitals in its conjugated π system?



A and B
will be the same

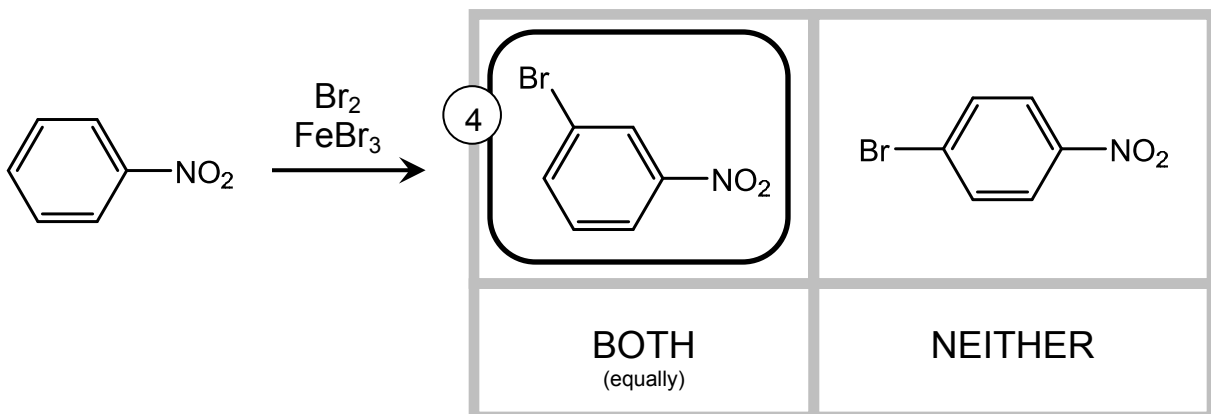
cannot determine

Molecule **B** has more sp^2 atoms in a row than molecule **A**; the 7 sp^2 -hybridized atoms in **B** will mix to form 7 molecular orbitals, while the 5 sp^2 -hybridized atoms in **A** mix to form just 5 molecular orbitals. All of these orbitals will fill the same space in the molecular orbital diagram, and this means that the diagram with more orbitals will have less space between them:

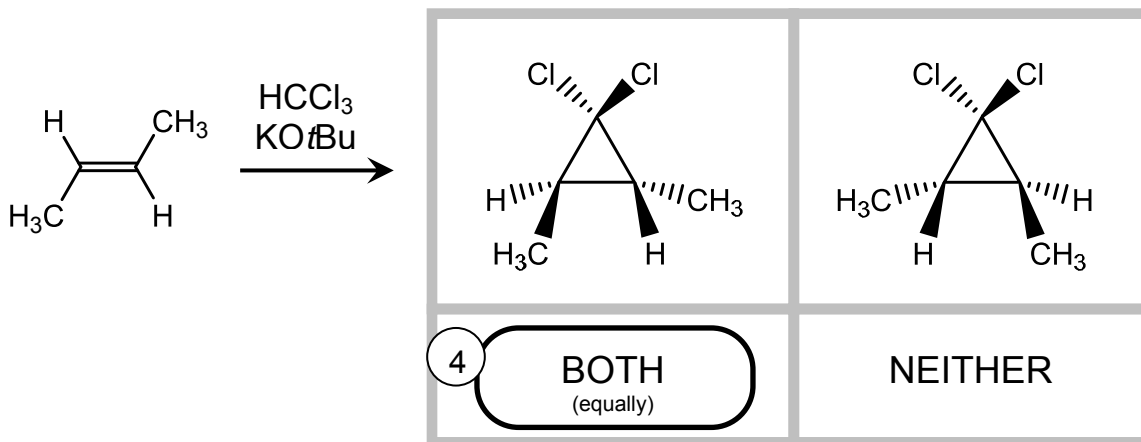


So **B** will have more orbitals, and **A** will have a larger HOMO-LUMO gap. The wavelength of absorbed light is inversely related to the energy gap between HOMO and LUMO (because $E=hc/\lambda$), so B will absorb at longer wavelengths.

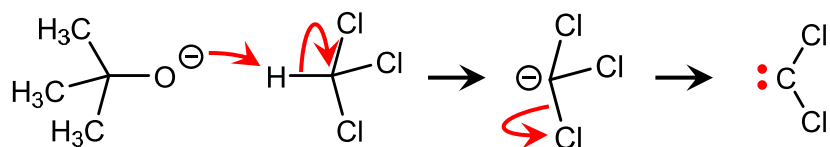
2. (24 pts) Each of the reactions on the following two pages is drawn with two possible products. If one of the two products predominates, circle that preferred product. If the two products are produced equally, circle "BOTH". If neither product would result from the reaction, circle "NEITHER". **Circle one answer only.**

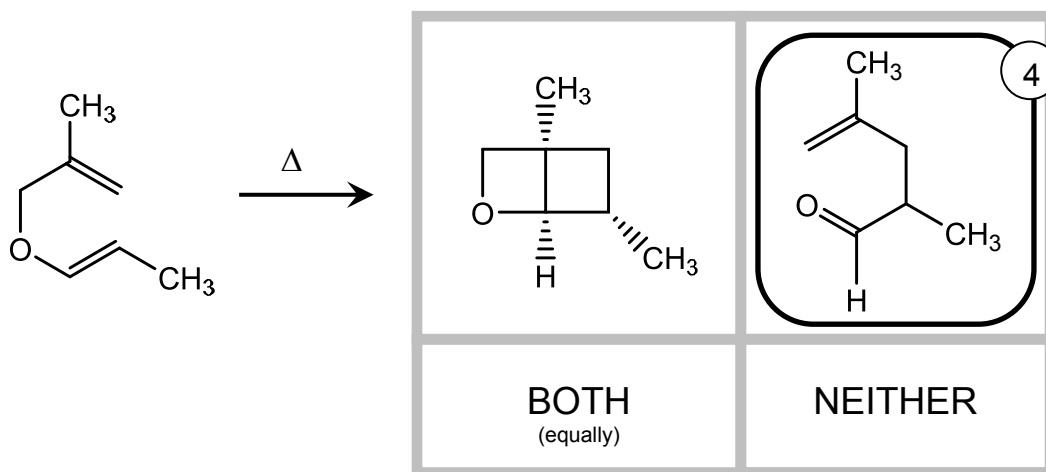
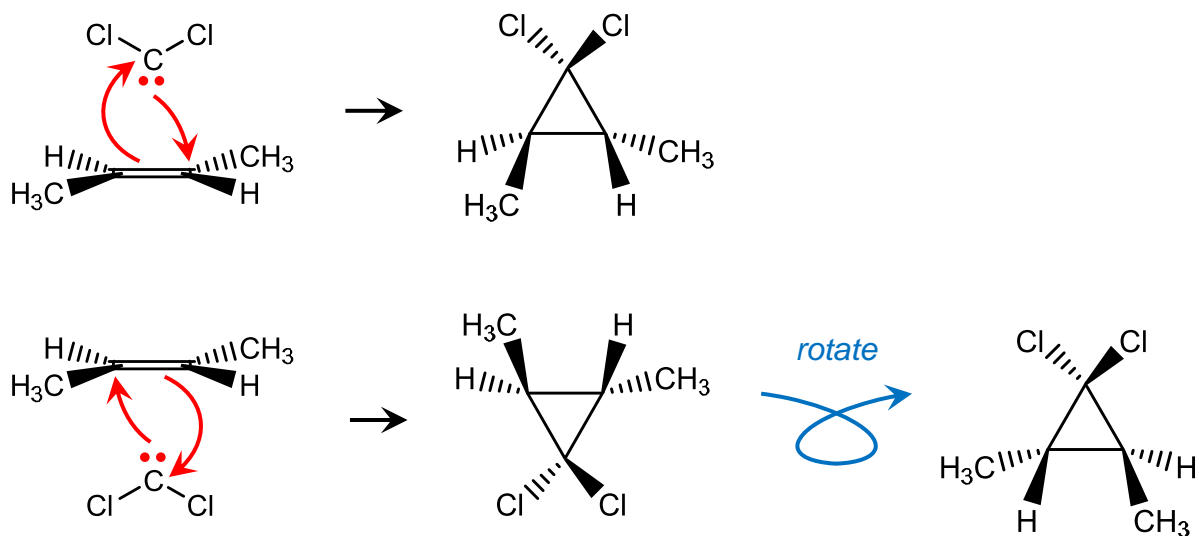


This reaction is an electrophilic aromatic bromination, and the $-\text{NO}_2$ group on the starting material is *meta*-directing. The *meta* product will be preferred.

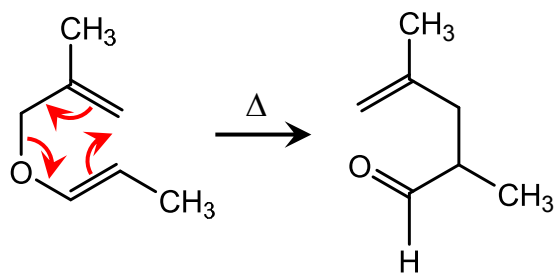


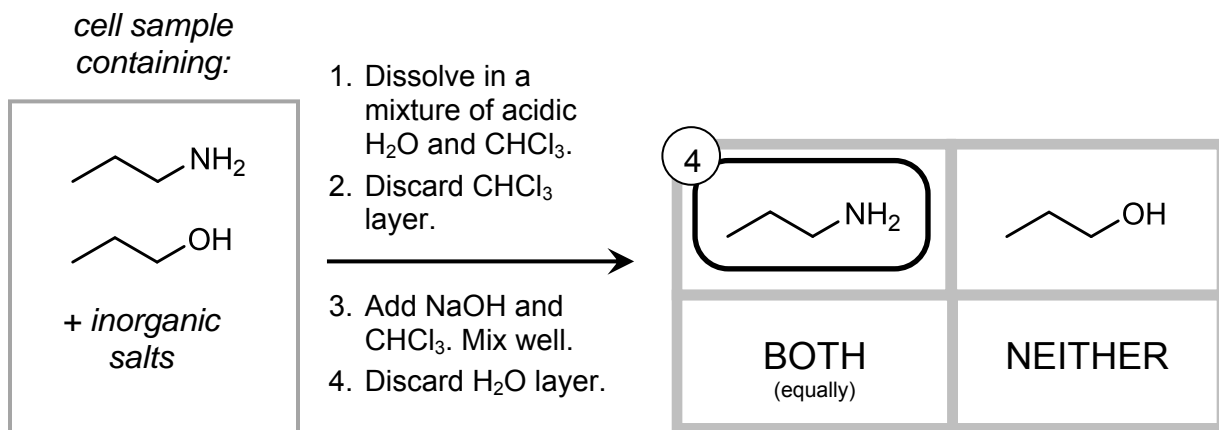
The reaction conditions generate dichlorocarbene, which can add to either face of the starting alkene to generate both product enantiomers.



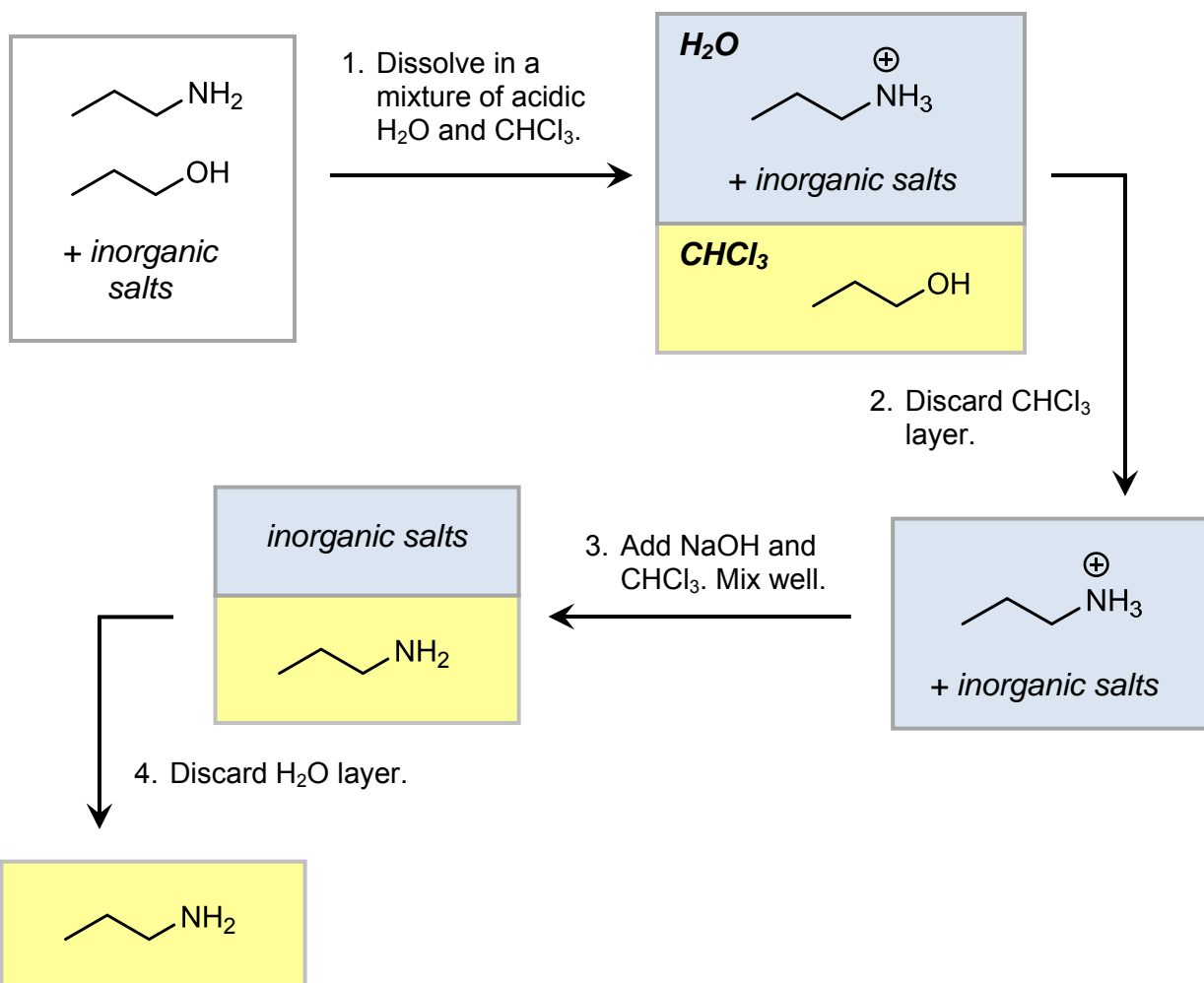


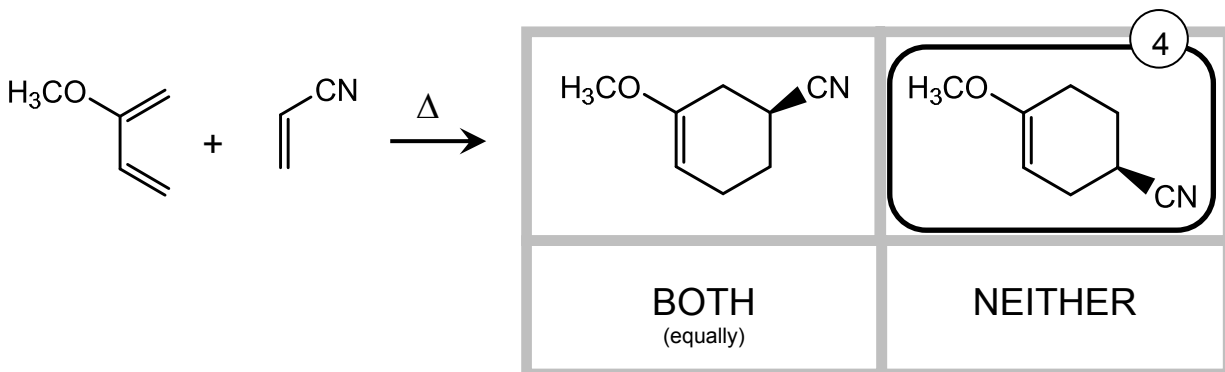
The first product would be generated by [2+2] cycloaddition of the two alkenes in the starting material. [2+2] cycloadditions are thermally forbidden (though photochemically allowed), so the product couldn't be generated by heat. The second product comes from Claisen rearrangement of the starting material.





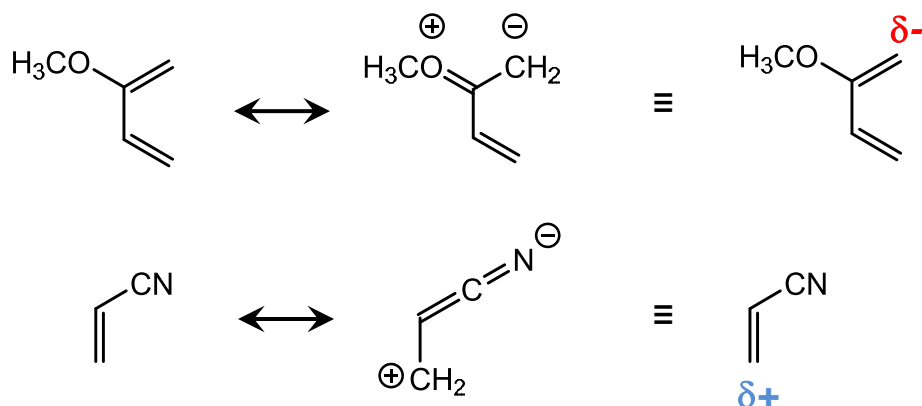
Here's what happens:



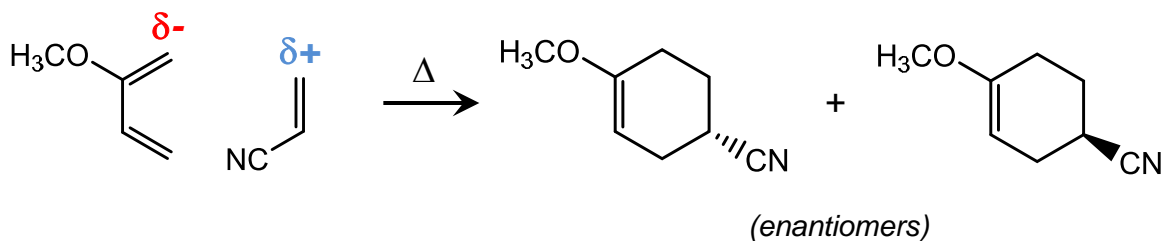


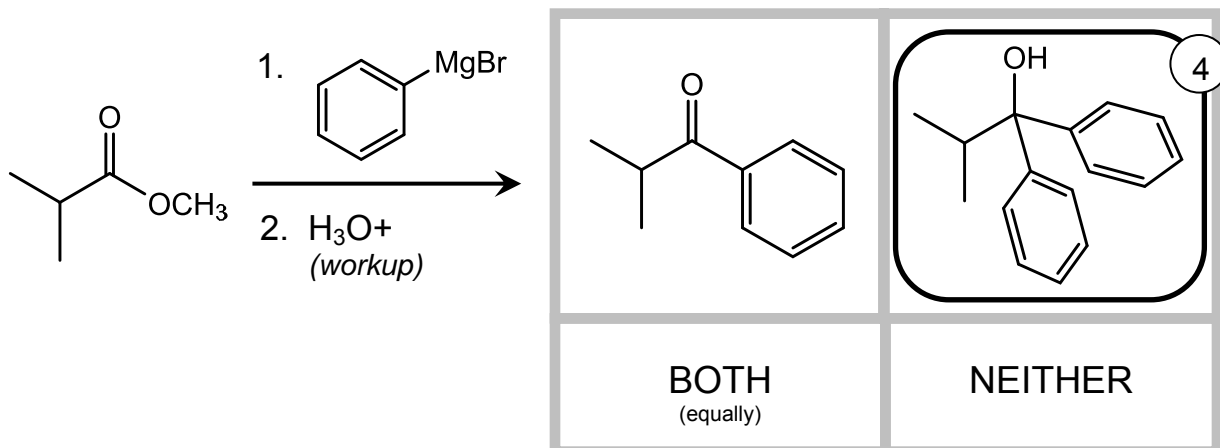
This is a Diels-Alder reaction. To solve Diels-Alder problems, I've got to arrange the diene and dienophile such that opposite partial charges line up, and that *p*-substituents on the dienophile are pointed *endo* (towards) relative to the diene.

Partial charges:

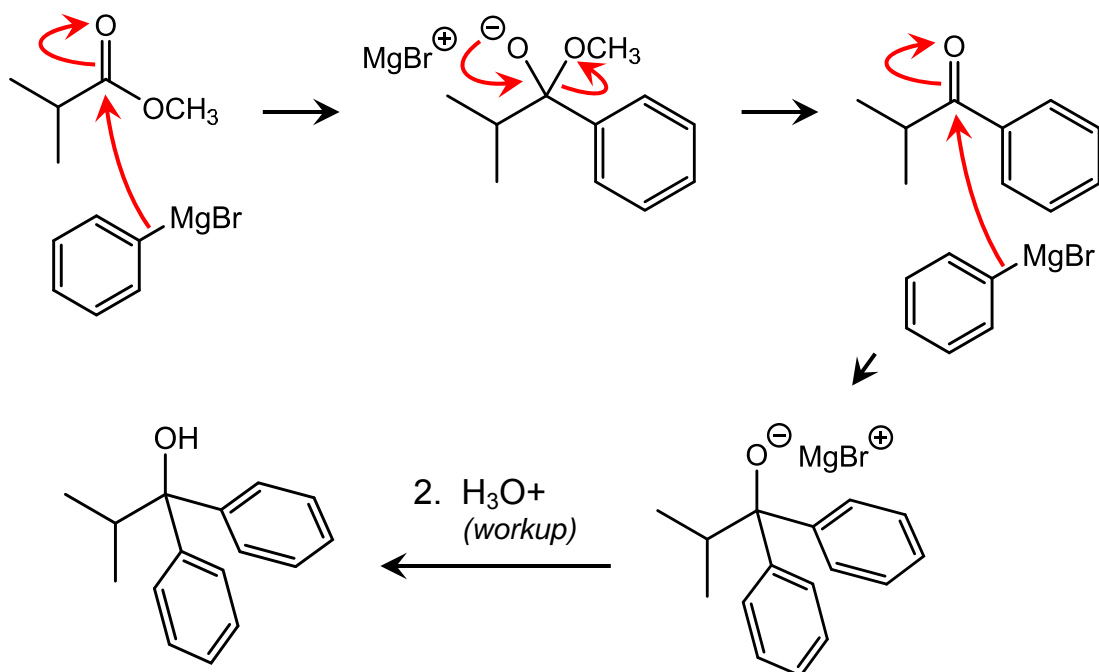


To align partial charges, I've got to flip one of the reactants vertically. In addition, the dienophile's π -substituent (the CN group) should be pointed towards the diene:

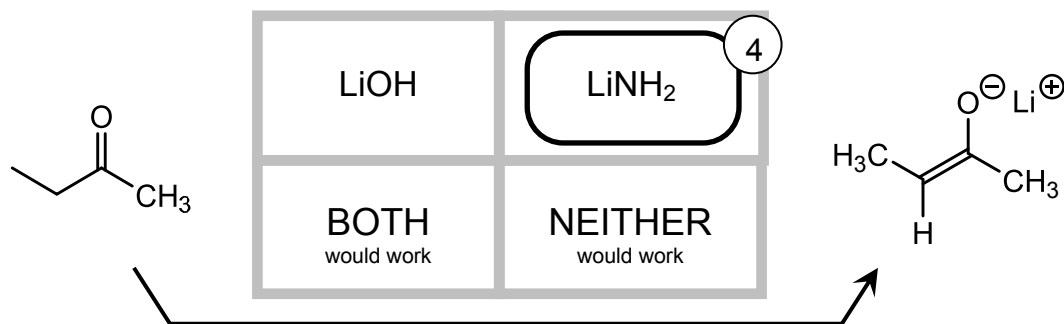




Grignard reagents add twice to esters, unavoidably. The first addition converts the ester to a ketone, which is more electrophilic than the original ester. It doesn't matter how many equivalents of Grignard reagent you use—it will always add twice.

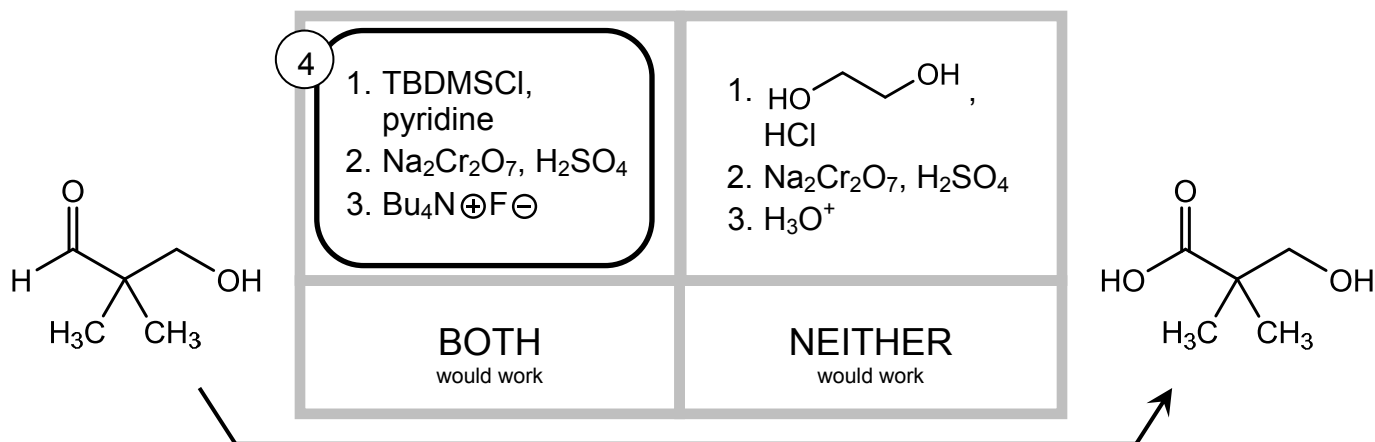


3. (16 pts) Each of the reactions below is drawn with two possible reaction conditions. If only one of the two reaction conditions would generate the given molecule as the major product, circle those conditions. If both sets of conditions would accomplish the reaction, circle "BOTH". If neither set of reaction conditions would succeed, circle "NEITHER". **Circle one answer only.**

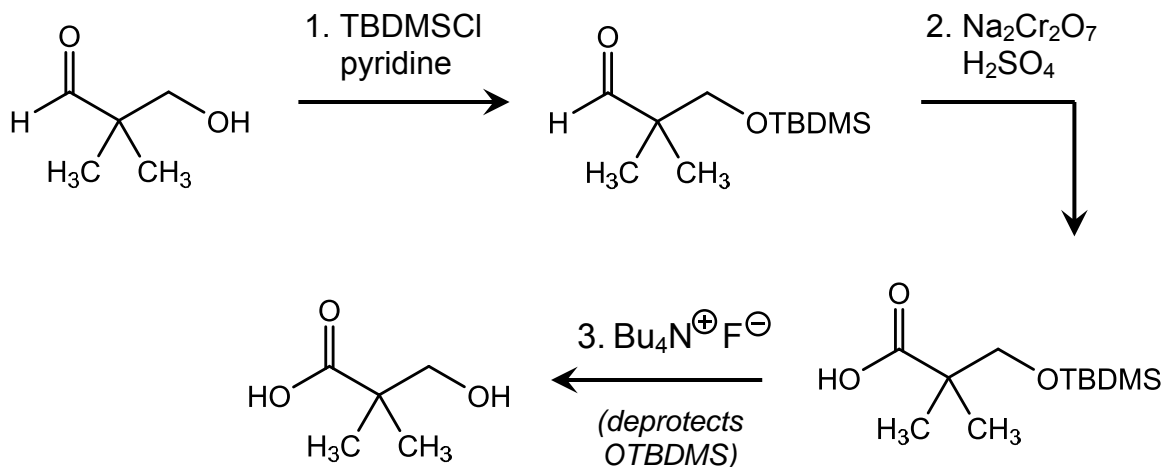


Both of the reagents shown are bases, and could potentially deprotonate our starting ketone. Our starting ketone will serve as the acid, with a $pK_a \approx 20$, and can only be protonated quantitatively by a base whose conjugate acid has a $pK_a > 20$. The pK_a of H_2O is just 15, so OH^- can't deprotonate the starting ketone quantitatively. (It can deprotonate it a little, enough to carry out enolate reactions. But it wouldn't make the enolate as a product.) On the other hand, the pK_a of NH_3 is 35, which means that NH_2^- is strong enough to deprotonate the ketone quantitatively.

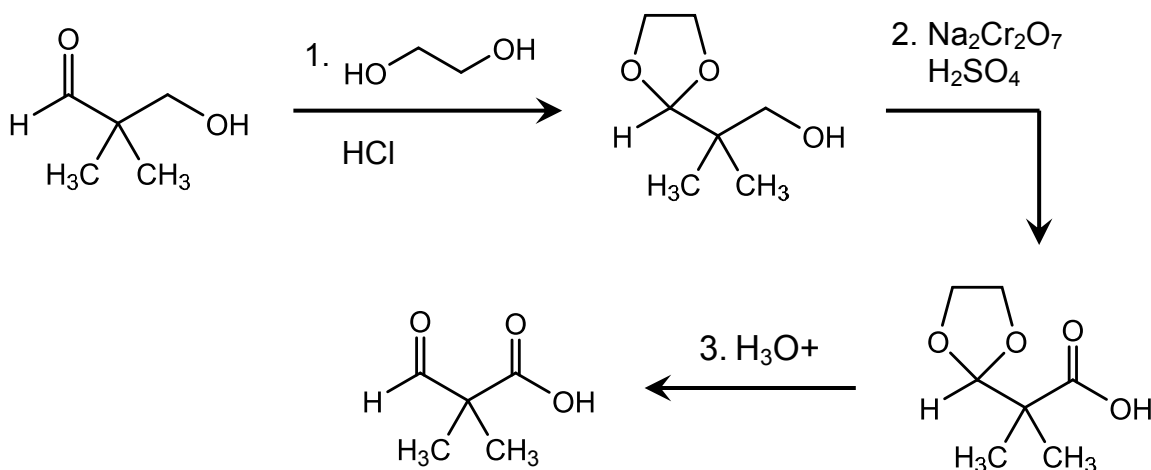
One question a few students asked me was, "is this enolate the one that would be made?" I think it would be—here, the (Z)-enolate puts the two most sterically demanding groups, the two methyl groups, on opposite sides of the enolate $C=C$ bond.



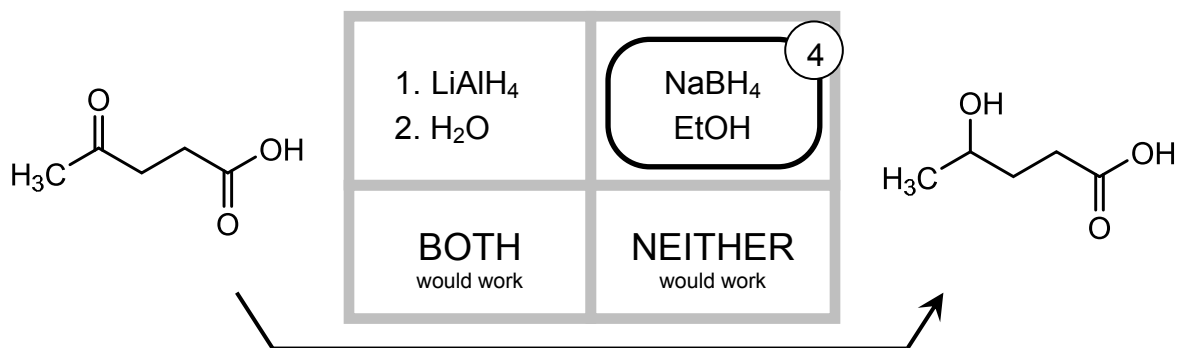
Both reaction sequences illustrate protecting group schemes, designed to execute chromate oxidation on just one side of the molecule. The sequence on the left protects the alcohol, to oxidize the aldehyde:



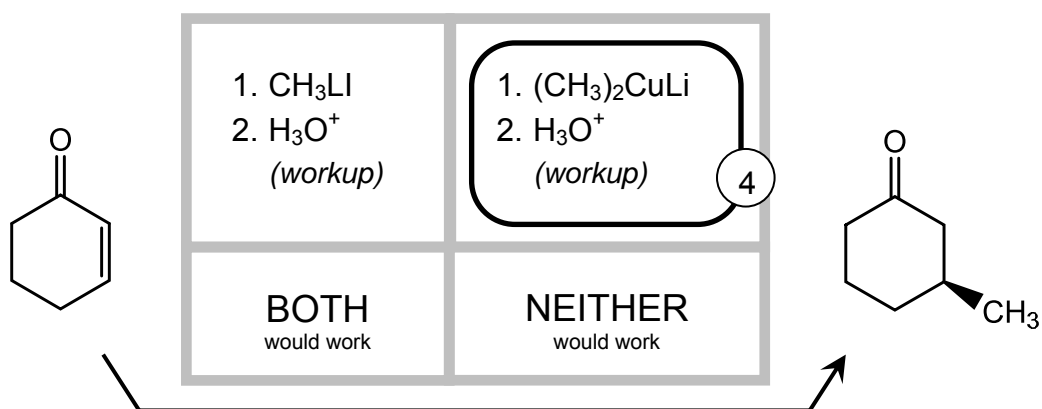
The second sequence protects the aldehyde, and would oxidize the alcohol instead:



A practicing synthetic chemist would probably question whether either protecting group could survive the harsh conditions of chromate oxidation—they would probably test this experimentally—but in principle, only the first sequence is designed to get us to the product shown in the problem.

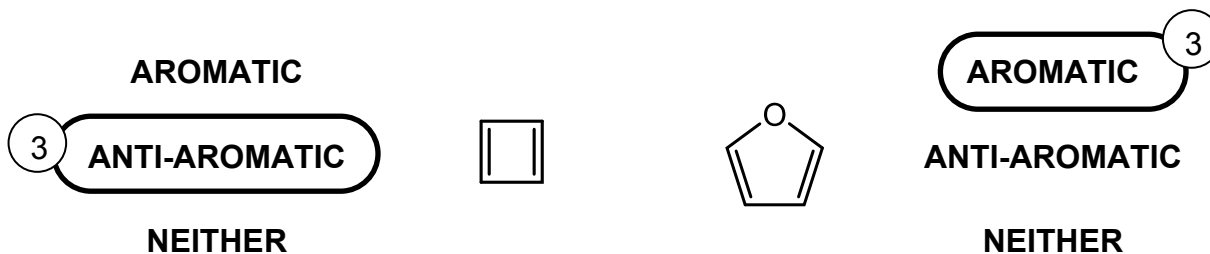


The two reaction conditions shown involve reducing agents, and both of the functional groups in our starting material *can* be reduced. But the product shows only the ketone being reduced, and not the carboxylic acid. This would occur only for a weak reducing agent like NaBH_4 , which exclusively reduces aldehydes and ketones, and not a strong reducing agent like LiAlH_4 .



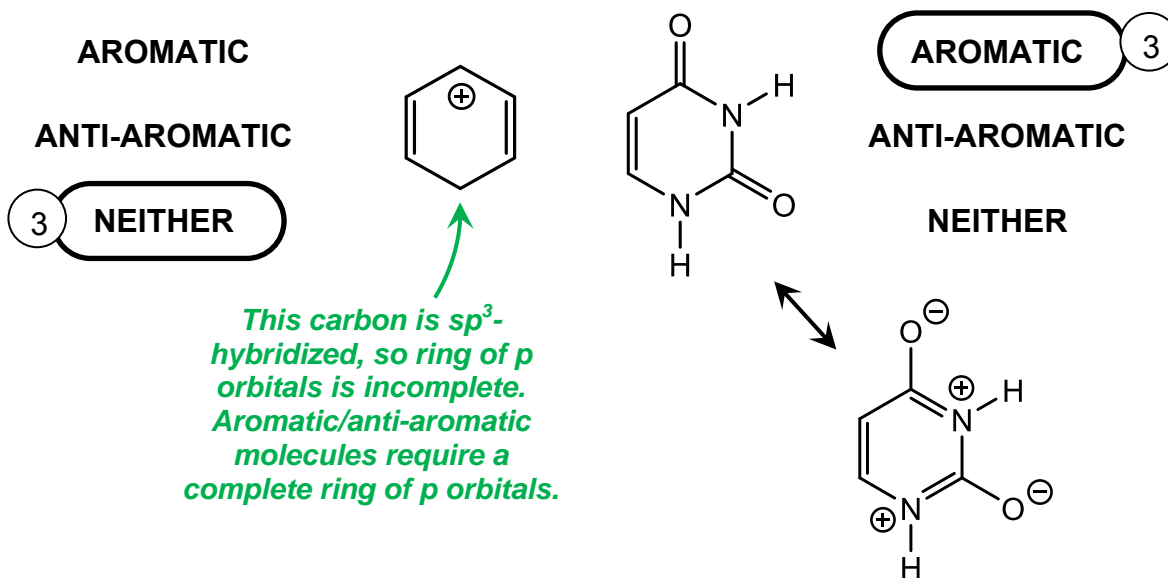
The product here shows 1,4-addition (also called conjugate addition, or Michael addition) of an alkylmetal to the starting material. Out of the two alkylmetal reagents shown, the first (alkyllithium) adds 1,2, and the second (dialkylcuprate) adds 1,4.

4. (12 pts) For each of the following molecules, circle whether the molecule is aromatic, anti-aromatic, or neither.



*4 π electrons.
Anti-aromatic.*

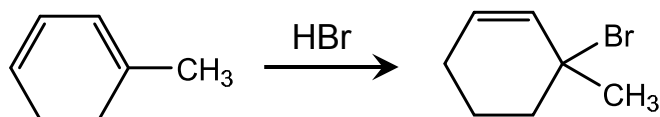
*6 π electrons—4 from the
two double bonds, and 2
from a lone pair on the
 sp^2 -hybridized oxygen.
Aromatic.*



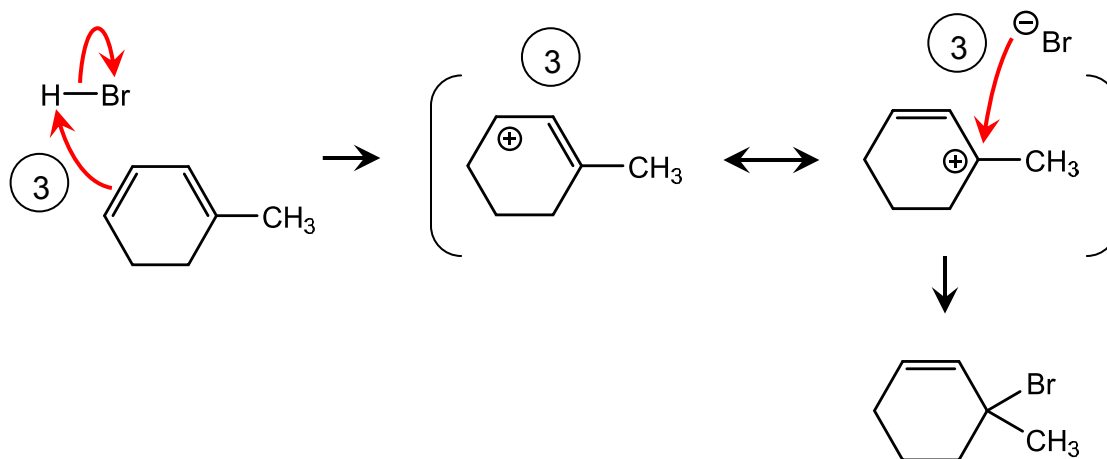
*This carbon is sp^3 -
hybridized, so ring of p
orbitals is incomplete.
Aromatic/anti-aromatic
molecules require a
complete ring of p orbitals.*

*If a molecule has an aromatic resonance
structure, it is aromatic. This molecule has a 6 π
electron resonance structure, so it's aromatic.*

5. (18 pts) **Draw a mechanism** (using “electron pushing”) for each of the reactions shown on the next page. Draw each mechanistic step explicitly; don't cheat by combining multiple processes in a single step, or by taking shortcuts. Use only the molecules shown in the problem.



Mechanism:



Rubric:

3 points for each arrow-pushing step.

3 points for intermediate.

Overall notes:

Overall, the minimum score for each step is zero; errors in a step cannot earn you negative points that count against another, correct step.

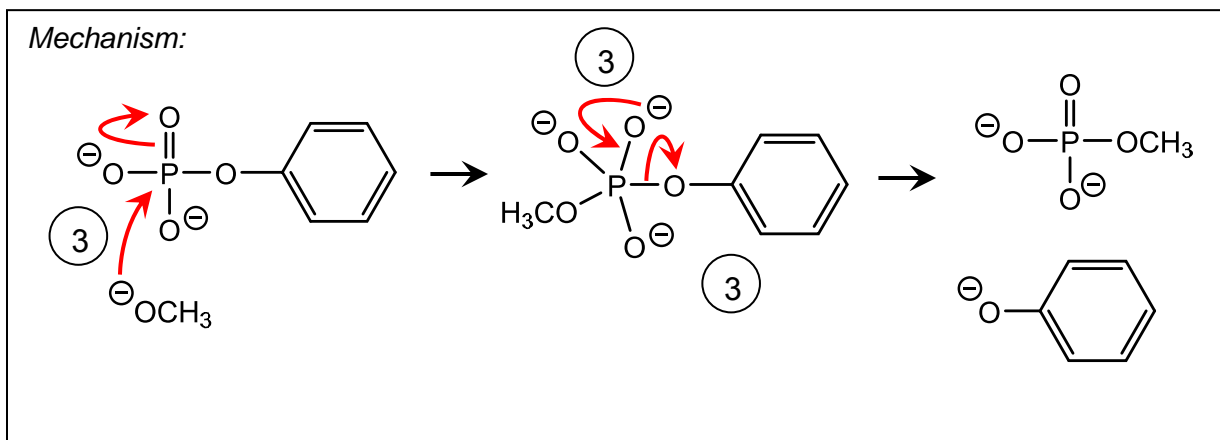
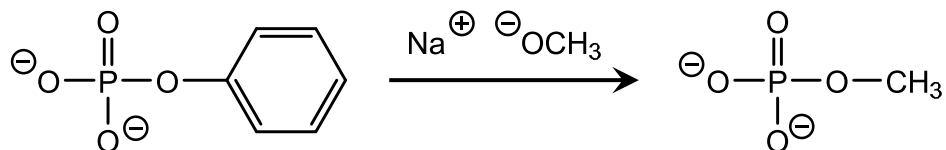
Proton transfer must be shown explicitly, with two arrows (one to proton, one from proton-acid bond). Can't abbreviate as "proton transfer", or draw an arrow on my writtin "HBr" (because it doesn't show the bonding electrons that have to be pushed).

The intermediate can be drawn as any resonance structure, or multiple ones, for full credit. Resonance is not a mechanistic "step"—we did not judge electron-pushing associated with resonance.

-2 points, for each arrow in each step, for errors (including omission) in drawing one arrow in a multi-arrow step. Arrow must start at an electron pair (either a bond or a lone pair), and end at nucleus or bond where electrons will newly interact.

-2 points for each error in charge, valency, structure, base, etc.; if error propagates, points are taken off only for initial error.

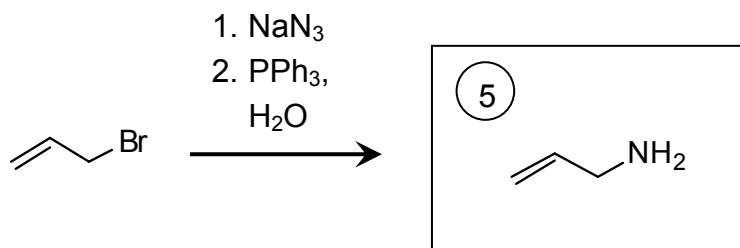
If you combined the two steps into one, you could get points for arrows that are in the rubric, but not for the intermediate you skipped.



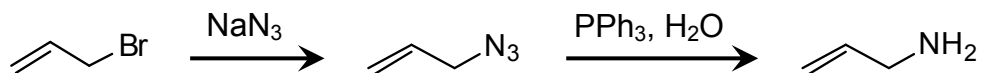
Rubric:

Same as previous part.

6. (20 pts) For each of the reactions on the next page, fill in the empty box corresponding to product. Give only one answer in each box. For reactions that you expect to yield multiple products, draw one major product. For reactions that yield multiple enantiomers, draw only one enantiomer in the box, and include the note “+ enantiomer”.



This is one method for making a primary amine. The synthetic route looks like:



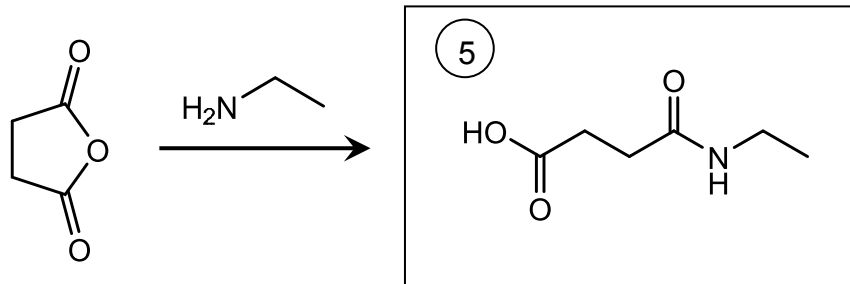
Rubric for this part:

5 points for correct structure.

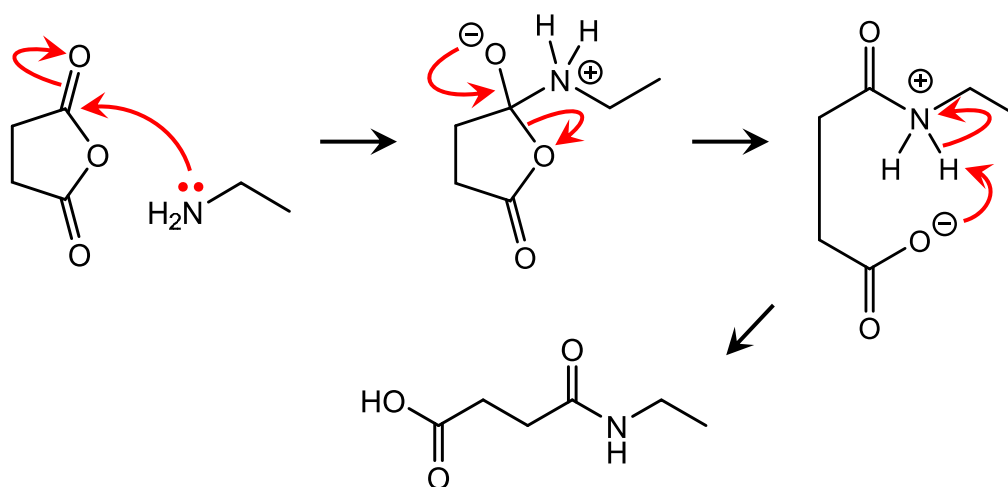
2 points partial for allyl azide.

2 points partial for propylamine (missing double bond).

-2 points for each clearly trivial structure mistake.



The starting material here is a cyclic anhydride. Anhydrides react with nucleophiles once, at either carbonyl group; this anhydride will react to open the ring:

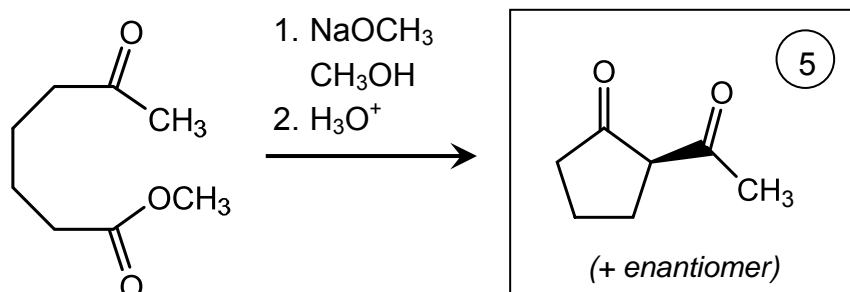


Rubric for this part:

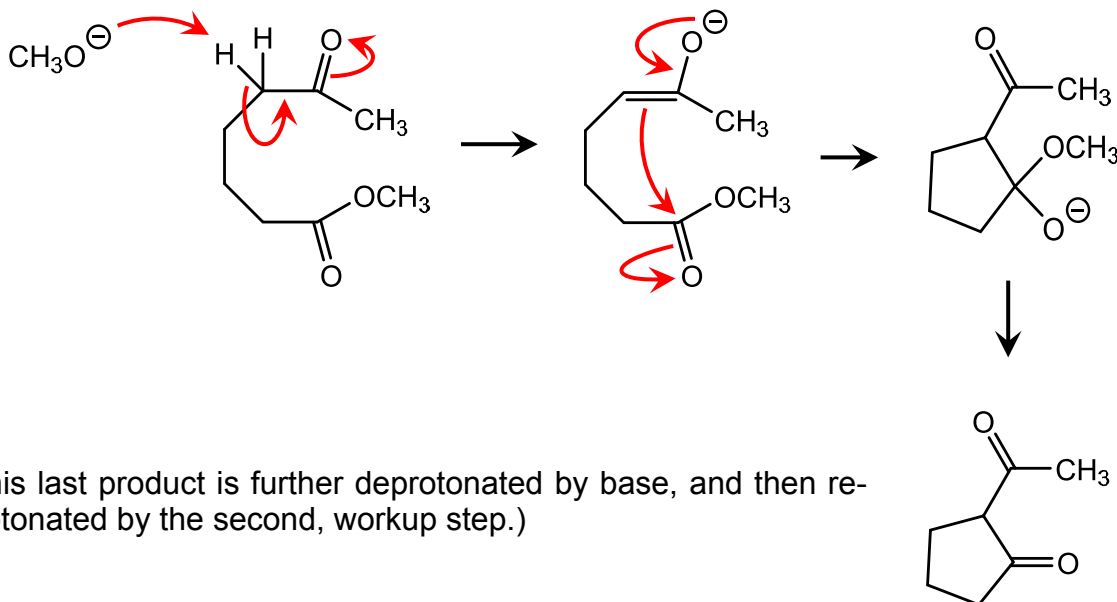
5 points for correct structure.

2 points for bis-amide.

-2 points for each clearly trivial structure mistake.



Our starting molecule has two different functional groups that could be deprotonated by a base to form an enolate—a ketone, and an ester. Out of those two, the ketone is more acidic, so it would be deprotonated preferentially. The ketone will be deprotonated at the more substituted carbon, if that leads to a reasonable product:



(This last product is further deprotonated by base, and then re-protonated by the second, workup step.)

Rubric for this part:

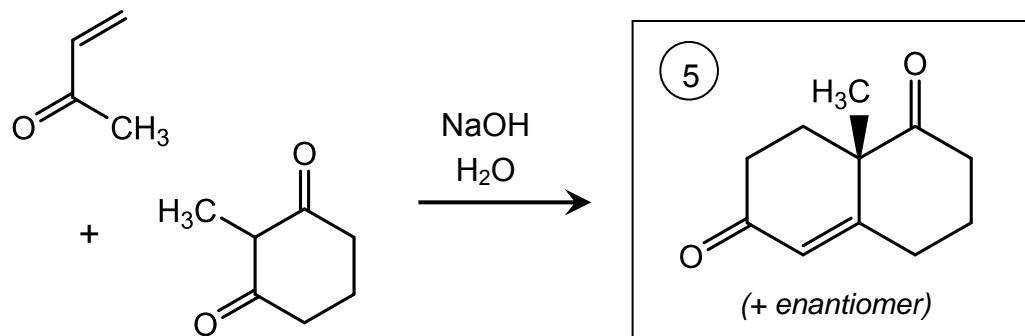
5 points for correct structure.

We did not grade the “+ enantiomer” on this problem.

4 points for 7-membered ring diketone.

3 points for ester-alcohol.

-2 points for each clearly trivial structure mistake (including incorrect number of carbons in the ring).



Rubric for this part:

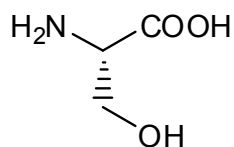
5 points for correct structure.

We did not grade the “+ enantiomer” on this problem.

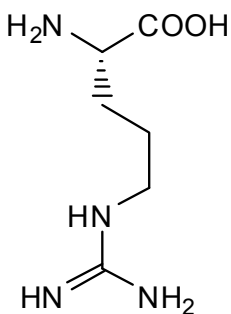
-2 points for each clearly trivial structure mistake.

7. (6 pts)

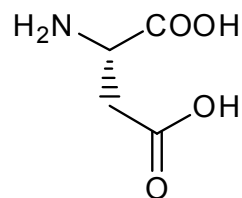
(a) Sort the three amino acids serine (Ser), arginine (Arg), and aspartic acid (Asp) in order of increasing isoelectric point (pI). Write their three-letter abbreviations in the appropriate boxes below.



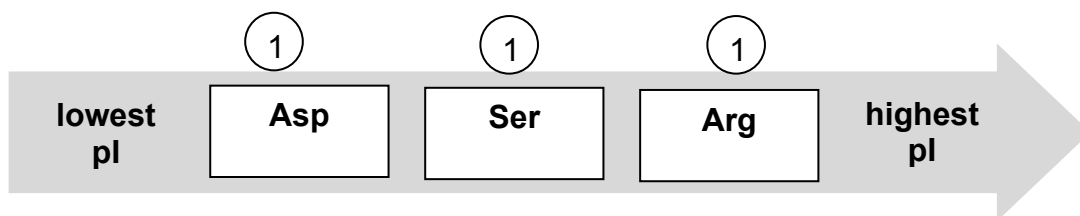
serine (Ser)



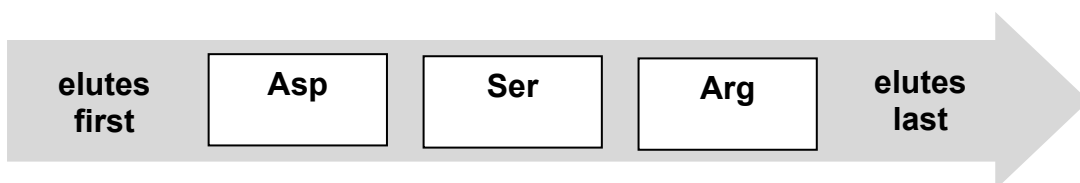
arginine (Arg)



aspartic acid (Asp)



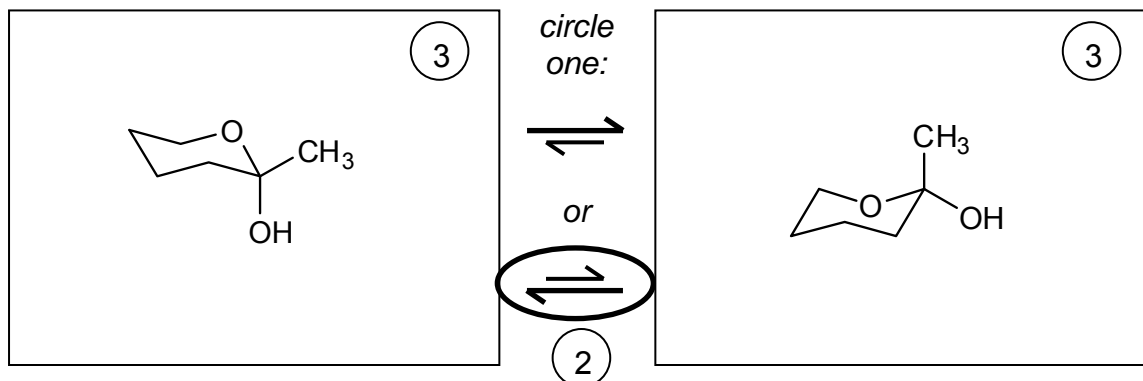
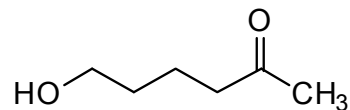
(b) If these three amino acids were analyzed by ion exchange chromatography, using an anionic column subjected to a solvent gradient of gradually increasing pH, what would be the order of elution of these three amino acids?



③ for either all three correct, or for answer the same as the student wrote for part (a)

8. (8 pts)

- a. 1-hydroxy-5-hexanone (shown at right) equilibrates with a cyclic hemiketal that can assume two different chair conformations. In the boxes below, draw those two hemiketal chairs. Then, indicate which conformation you think is more stable.



*for choosing equilibrium
towards axial -OH
(whichever direction that is)*

At the hemiketal carbon, the ring has two substituents: a $-CH_3$, and an $-OH$. The $-CH_3$ group is slightly more sterically demanding, so it prefers to be equatorial. Meanwhile, the $-OH$ group benefits from the anomeric effect if it is axial. Both of these effects combine to make the second chair above more stable than the first.

Rubric:

3 points for each chair structure.

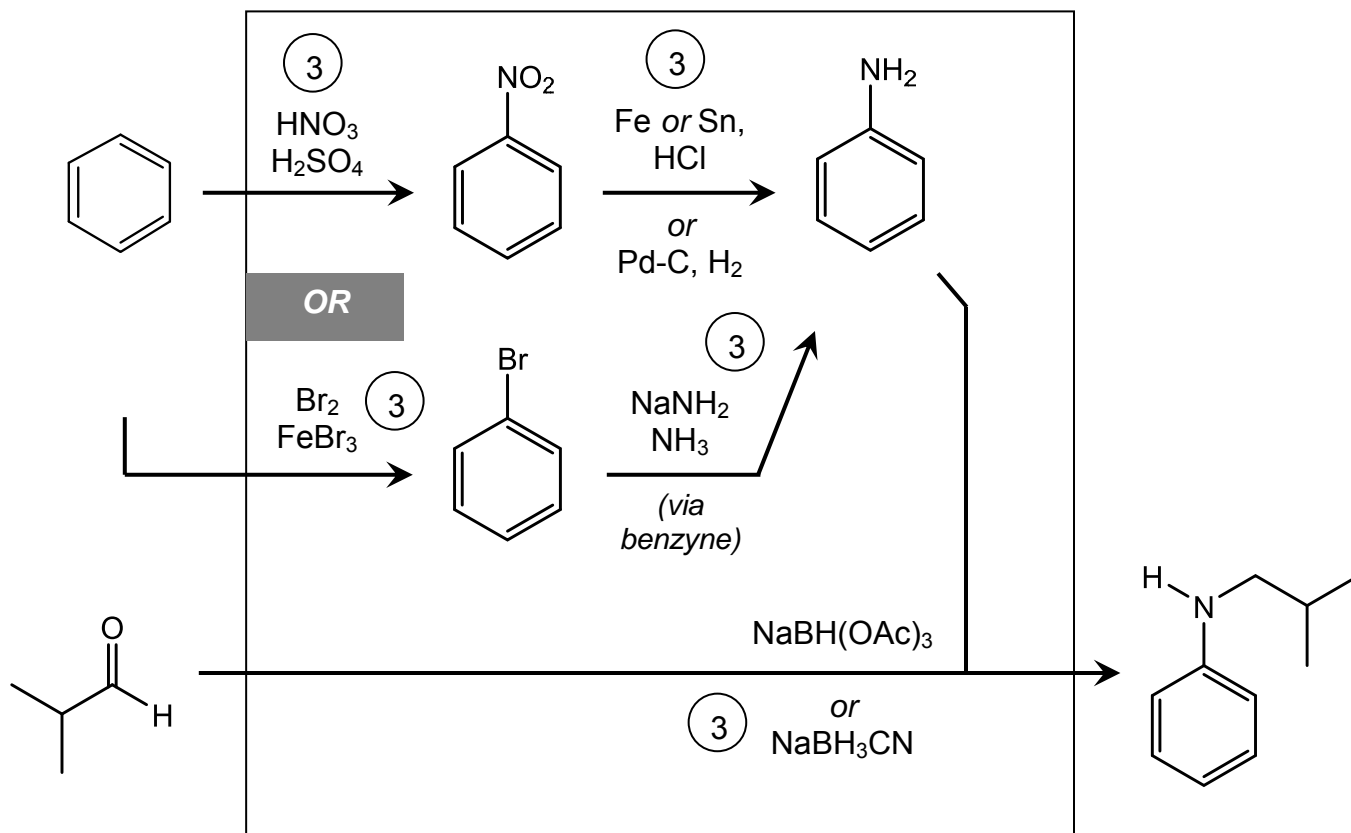
1 point partial for other sized cycle, or for omitting methyl or -OH.

-2 points for each trivial structural mistake.

2 points for correct equilibrium arrow.

Full credit for arrow pointing towards any product with axial -OH or equatorial - CH_3 .

9. (20 pts) Each of the syntheses shown below can be accomplished in a few steps. For each synthesis, fill in the empty boxes with any appropriate reagents (or sets of reagents) and synthetic intermediates that can be used in the synthesis of the drawn product from the starting material(s).



General rubric for synthesis problems:

Each synthesis require tasks, listed below. Each task is judged separately, and does not require that the synthesis makes sense, or that other tasks are correct.

- 1 point for each minor error in structures or reagents; if error propagates, points are taken off only for initial error.
- 2 points if step reagents are incorrect, but reaction could otherwise be accomplished with correct reagents.

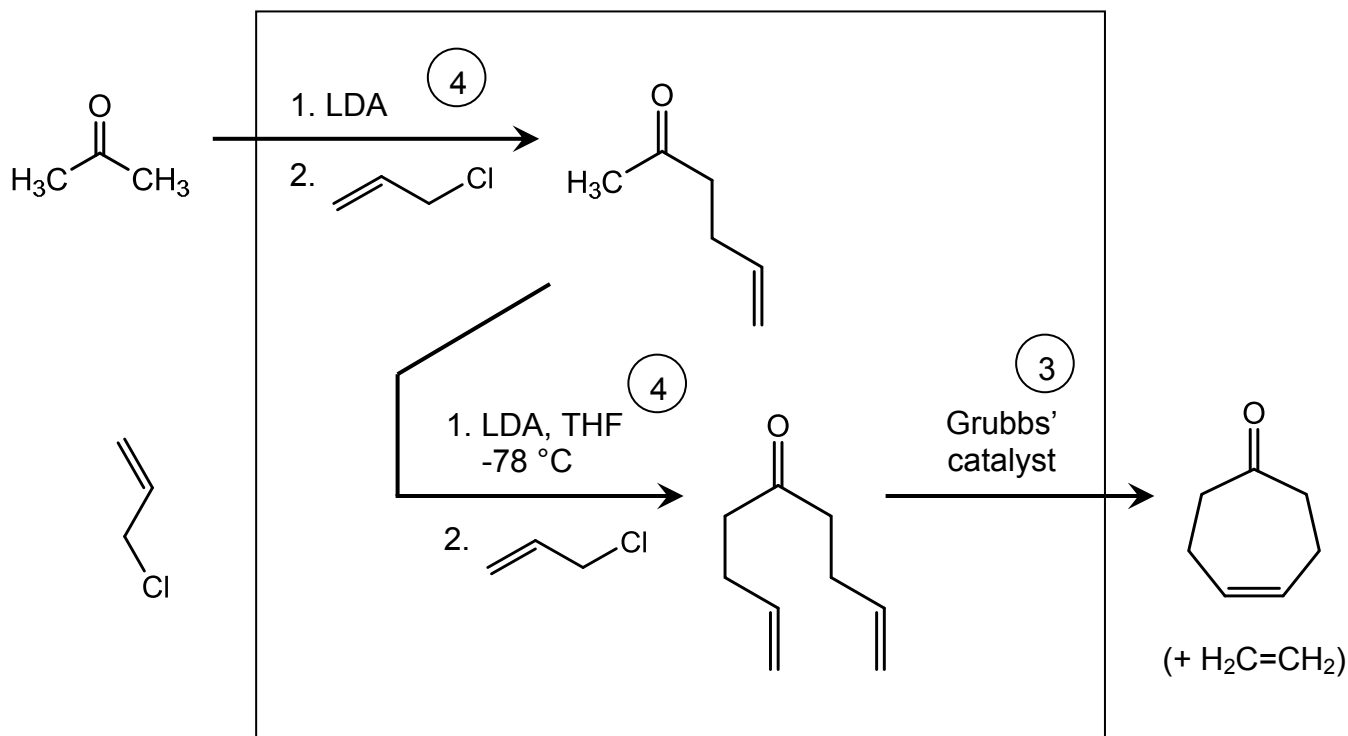
Task 1. Synthesize aniline. (6 points.)

You could do this a couple of ways:

- Electrophilic nitration of benzene (3 points) followed by reduction to the amine (3 points).
- Halogenation of benzene (3 points) followed by substitution by amide via benzyne (3 points).

Task 2. Reductive amination to generate product. (3 points.)

No partial credit for an S_N2 option, in either direction; oligo-alkylation will result.



Task 1. First α -alkylation w/ allyl chloride. (4 points.)

Pretty much any base/allyl chloride conditions will work. NaOH, NaNH₂, LDA will all generate reactive enolate.

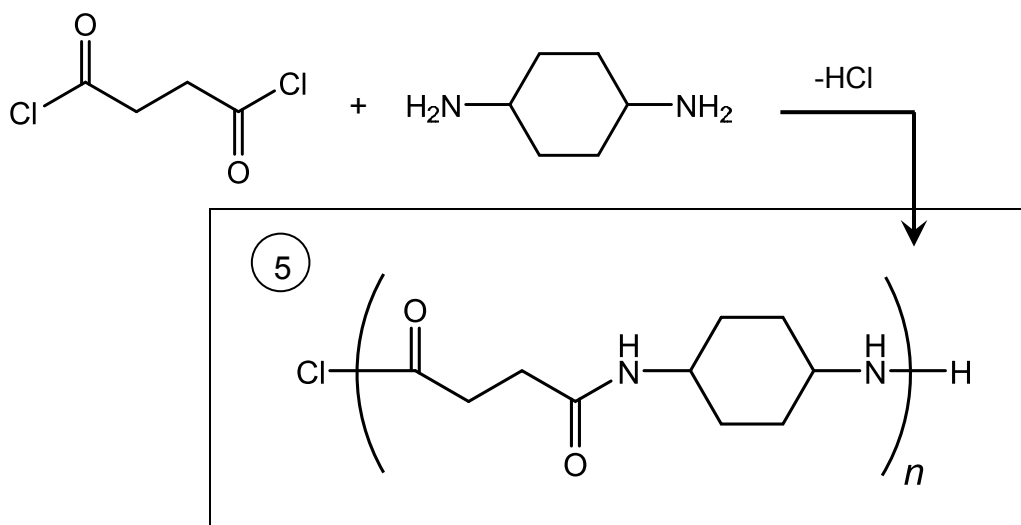
Task 2. Second α -alkylation w/ allyl chloride. (4 points.)

Requires formation of kinetic enolate; 2 points partial for any other enolate-forming conditions.

Task 3. Ring-closing metathesis. (3 points.)

10. (17 pts)

- a. For each of the polymer syntheses proposed on the next page, draw the polymer product using bracket notation (“[-M-]_n”). If there is a part of the polymer structure that isn’t known (e.g., the initiating or terminating group), draw this as a squiggle in your structure.



Condensation polymerization yields an alternating copolymer of the two monomers.

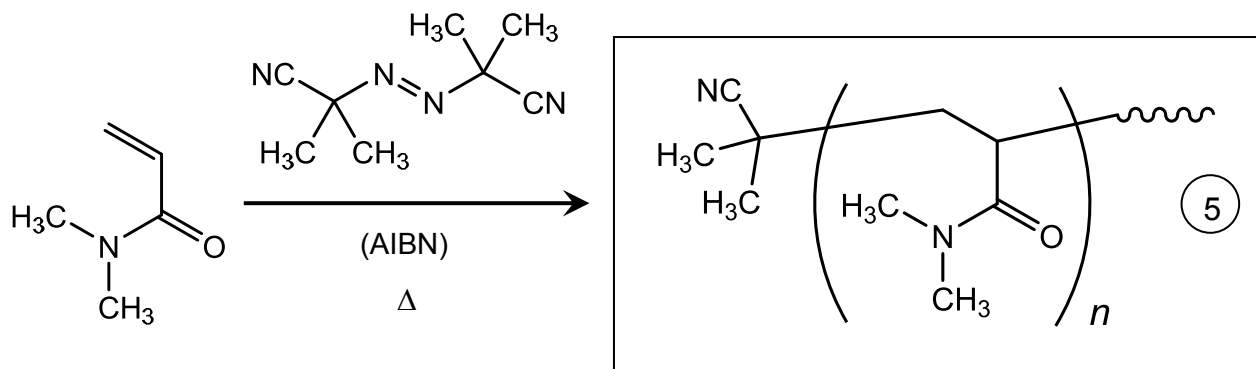
Rubric for this part:

5 points for correct structure.

2 points partial for alternating monomer structure.

2 points for bracket placement.

1 point for termini.



Free radical polymerization starts with a cyanopropyl radical. There are a few different termini structures that can form from radical polymerization, so we didn't grade that, but the initiator group is known.

Rubric for this part:

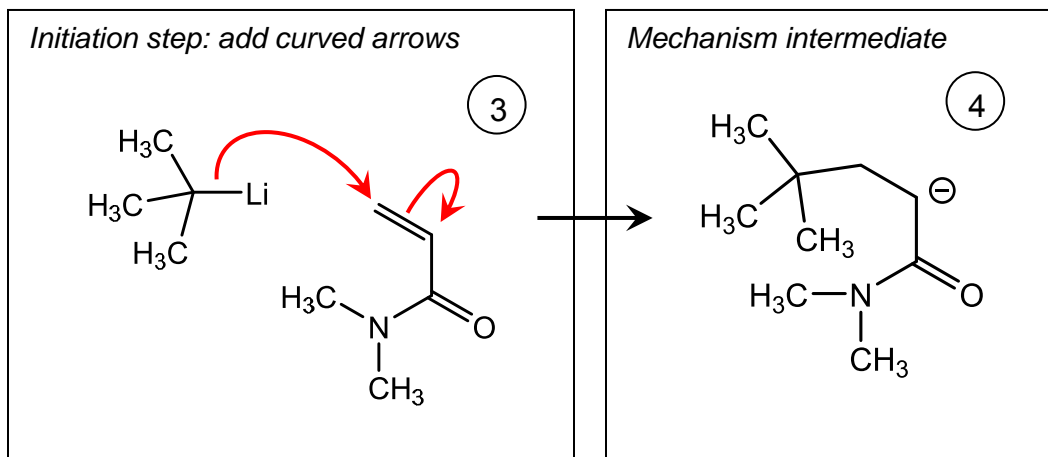
5 points for correct structure.

2 points partial for monomer structure.

2 points for bracket placement.

1 point for cyanopropyl initiator group.

- b. If the second polymerization above were initiated with *tert*-butyllithium instead of with AIBN, the mechanism of vinyl polymerization would be different. In the box below, **add curved arrows** (using “electron pushing”) that shows how *t*-BuLi would initiate polymerization. Then draw the intermediate formed from this mechanistic step.



Rubric:

3 points for each arrow-pushing step.

1 point partial for drawing just one arrow correctly out of 2. Both arrows must start at an electron pair. Arrows must be double-barbed.

4 points for intermediate.

-2 points for trivial error (in charge or structure).