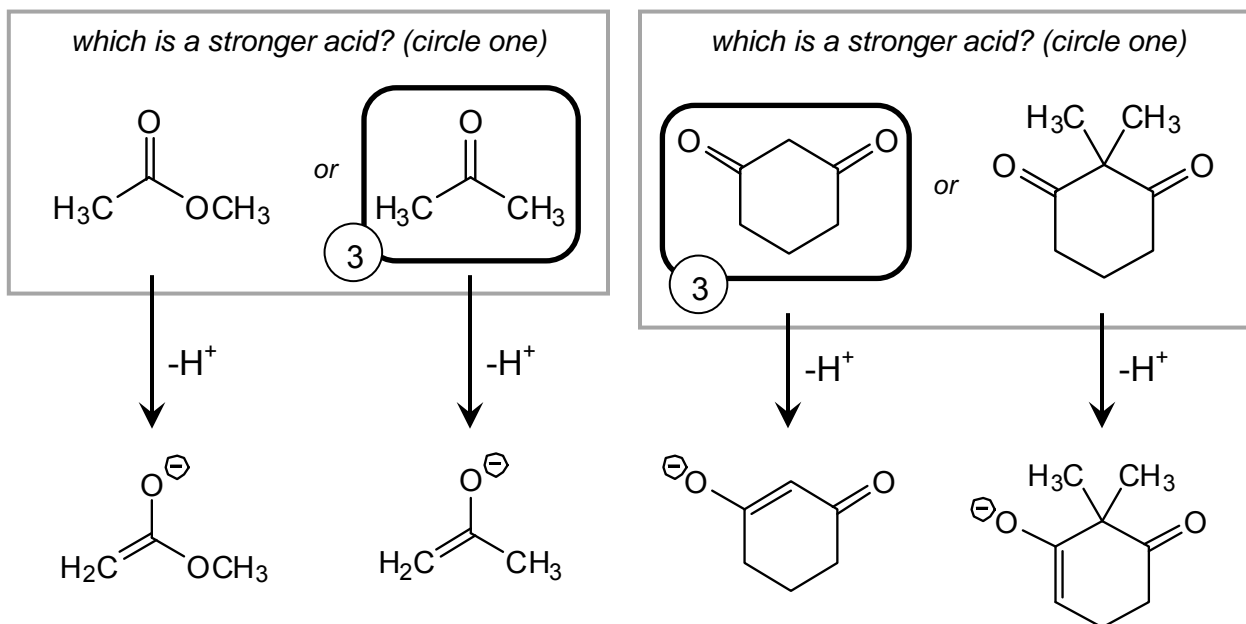


**Exam 3
Answer Key**

Exam 3 Mean:	67
Exam 3 Median:	67
Exam 3 St. Dev.:	15

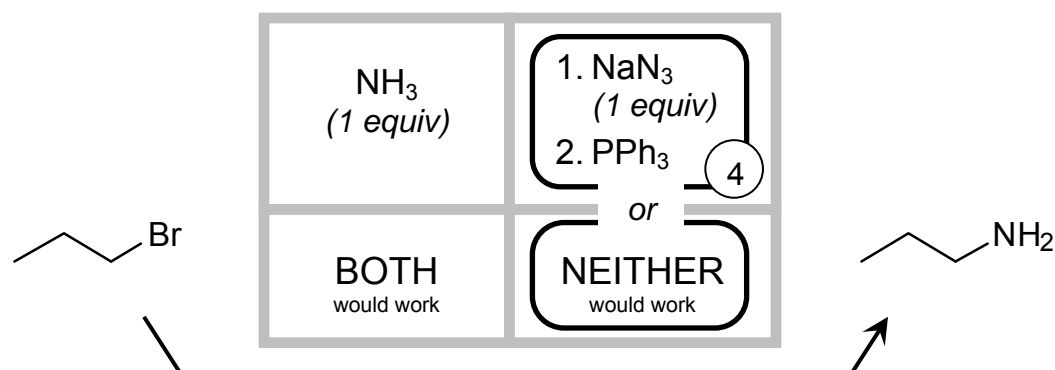
1. (6 pts) Each of the carbonyl-containing compounds below is acidic, and can be deprotonated to form an enolate anion. For each pair, **circle the stronger acid**.



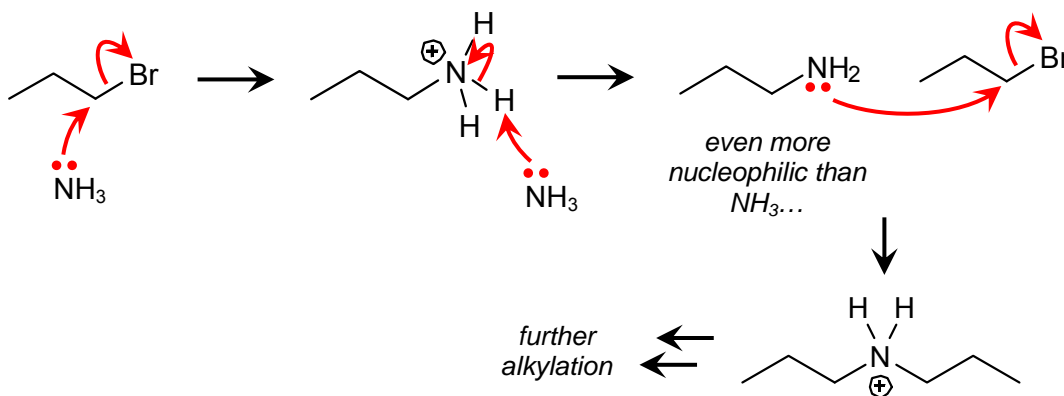
Of these two enolates, the one on the left is less stable because π -donation from the ester oxygen destabilizes the negative charge. That makes the acid on the right more acidic (because it leads to the more stable enolate).

The enolate on the left is more stable because it has more resonance structures. The acid on the right can't be deprotonated between the two carbonyls, so it's less acidic.

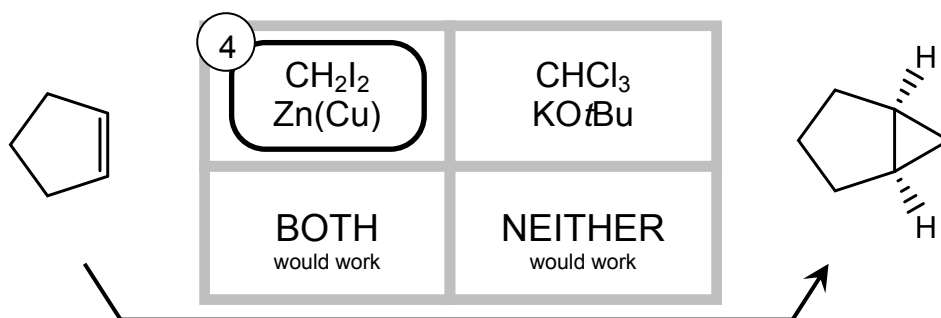
2. (20 pts) Each of the reactions below is drawn with two possible reaction conditions. If only one of the two reaction conditions would generate the given molecule as the major product, circle those conditions. If both sets of conditions would accomplish the reaction, circle "BOTH". If neither set of reaction conditions would succeed, circle "NEITHER". **Circle one answer only.**



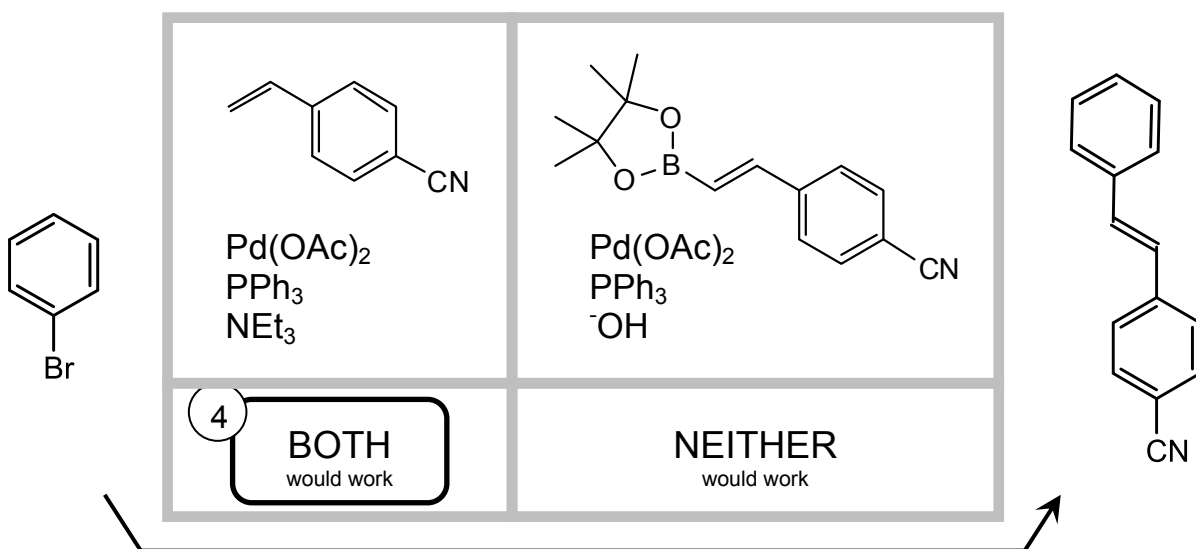
The method on the left does lead to nucleophilic displacement of $-Br$ by NH_3 . The problem is that, once that displacement occurs, it is nearly impossible to prevent the resulting alkylamine from alkylating again:



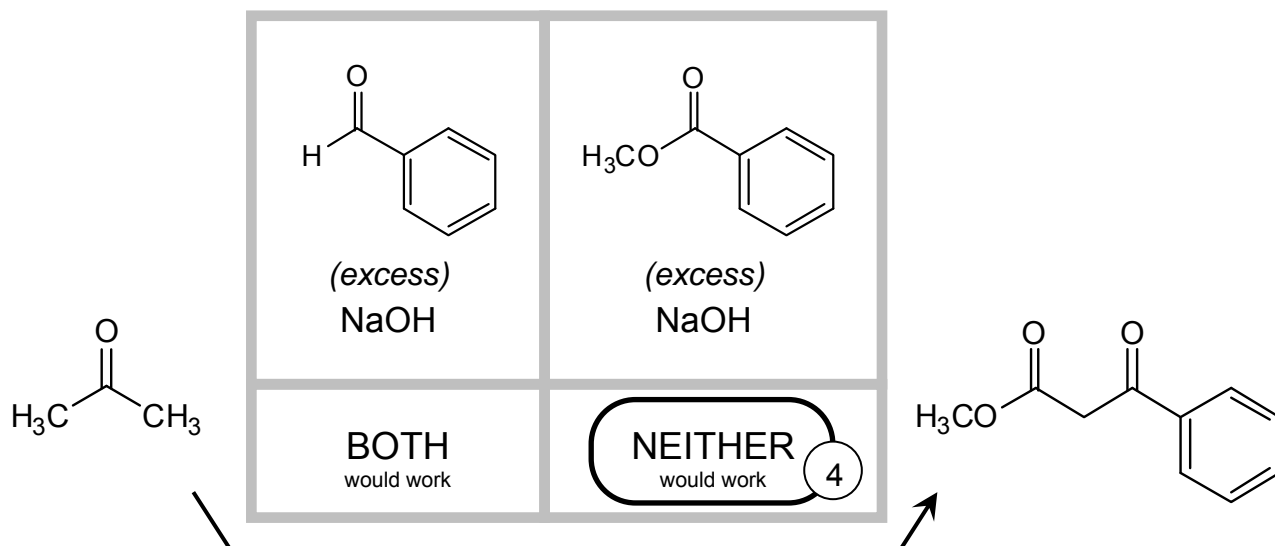
The sequence of N_3^- and PPh_3 , on the other hand, selectively forms the mono-alkylated amine.



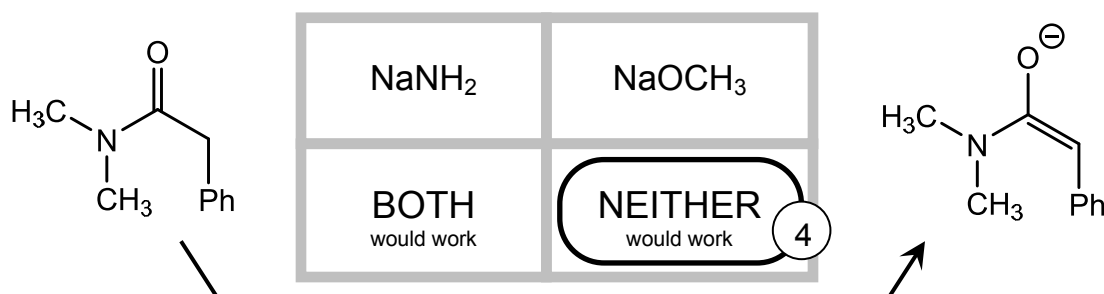
Both of these sets of conditions perform cyclopropanation of an alkene, via addition of a carbene. The conditions on the left add a $:CH_2$ group; the conditions on the right add a $:CCl_2$ group. (Your exam had a typo in the right-hand box, that showed CH_2Cl_2 instead of $CHCl_3$; these conditions would do nothing, so same answer.)



The conditions on the left correspond to the Heck reaction, and those on the right to the Suzuki reaction. Both succeed.

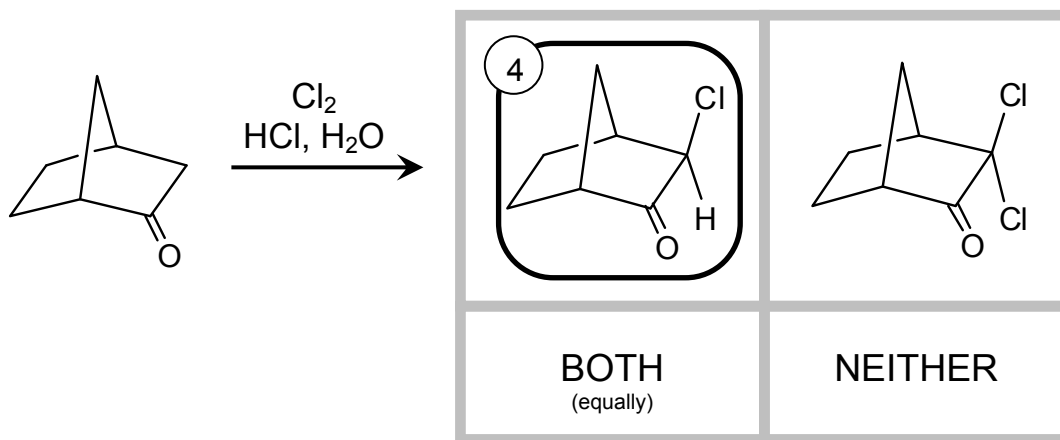


The β -keto ester product is a “synthon” for a Claisen condensation, in which an ester enolate reacts with another ester. That doesn’t match our acetone starting material, which isn’t an ester. So, neither of these methods would work.

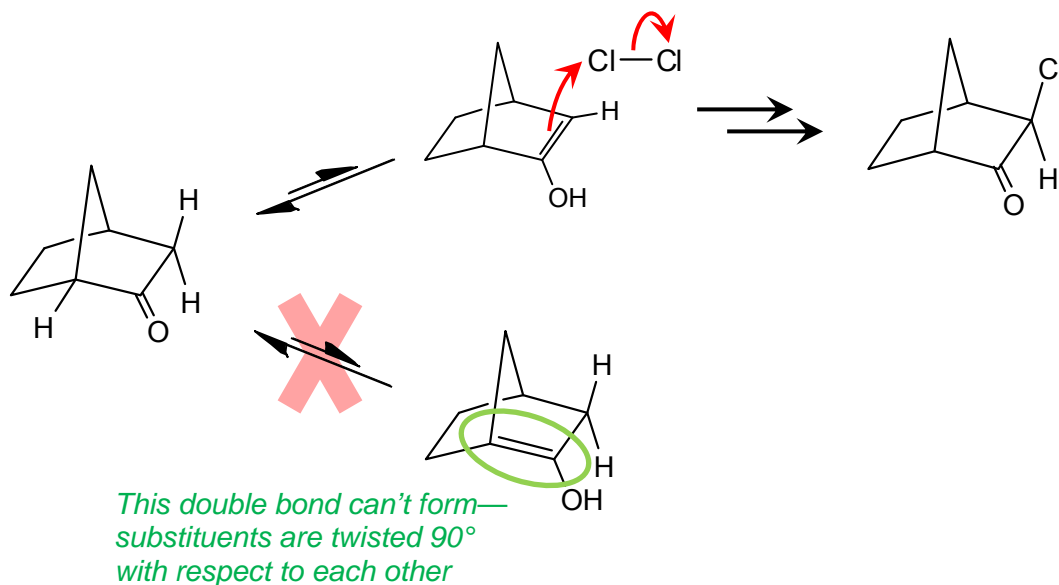


Out of the two bases shown in this problem, only one, NaNH_2 , is strong enough to deprotonate our amide quantitatively. But it will form the (Z)-enolate, not the one I’ve drawn.

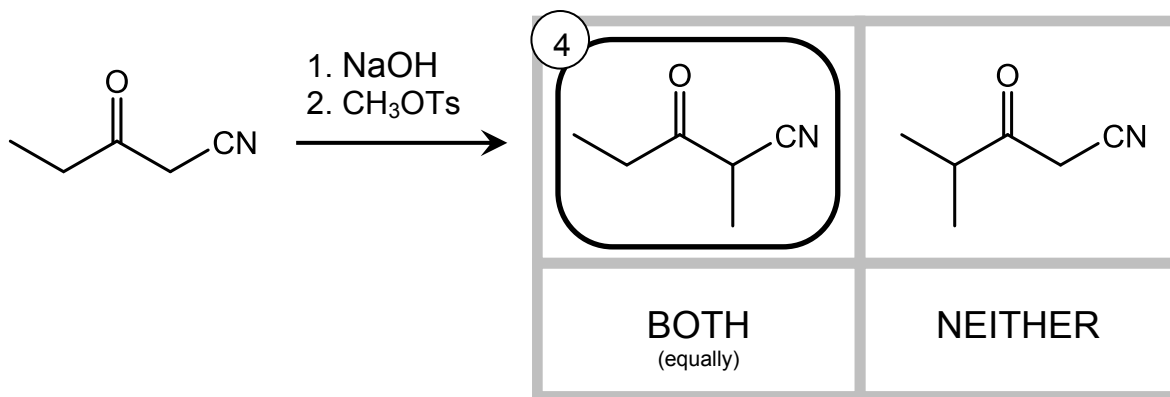
3. (16 pts) Each of the reactions on the next page is drawn with two possible products. If one of the two products predominates, circle that preferred product. If the two products are produced equally, circle “BOTH”. If neither product would result from the reaction, circle “NEITHER”. **Circle one answer only.**



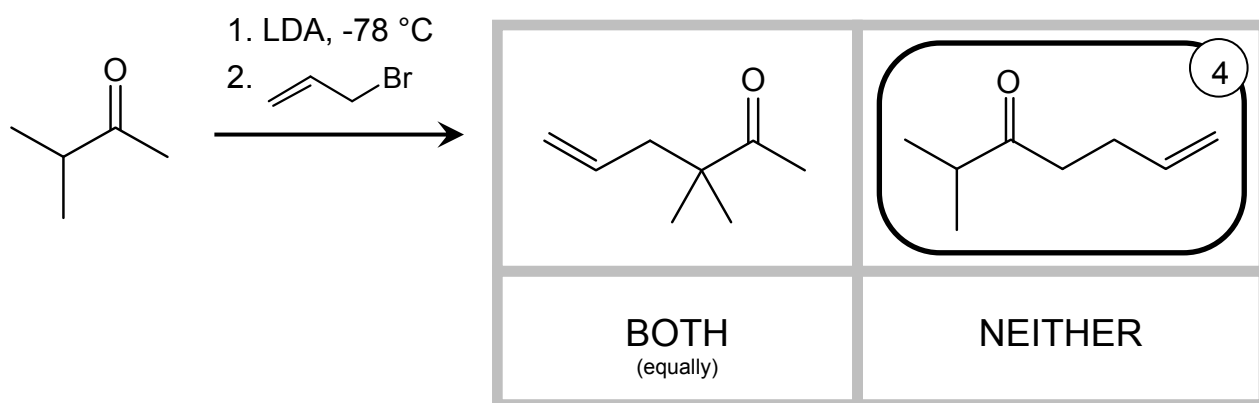
These reaction conditions—molecular halogen and acid—will halogenate carbonyl containing molecules α to the carbonyl, via an enol (rather than an enolate, which can only be formed in base). There are carbons on either side of the carbonyl group, but only the one on the right can form an enol; the carbon on the left is twisted relative to the plane of the carbonyl, such that an enol double bond can't be formed:



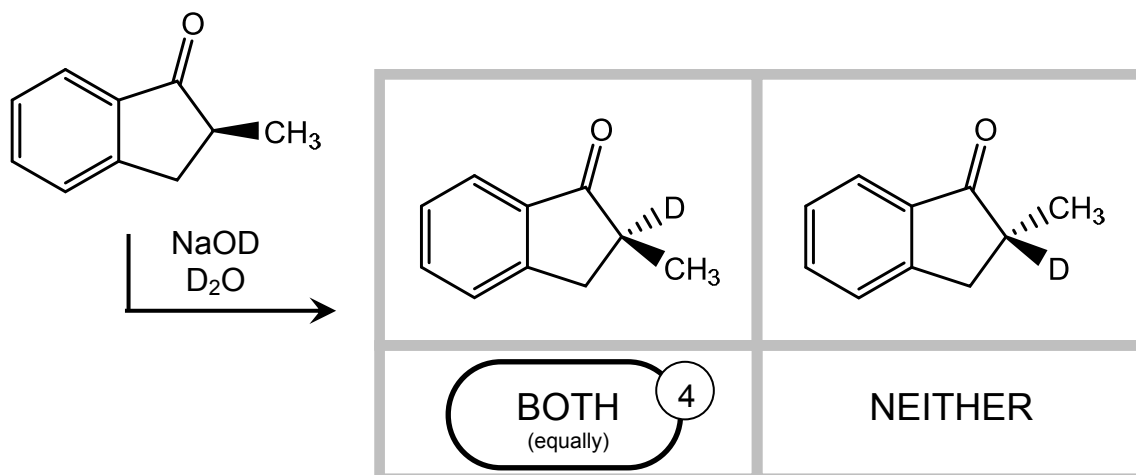
Once the enol is chlorinated at the α -carbon, any further chlorination fails because the enol is a worse electron donor.



The protons on the carbon on the right are much more acidic than typical enolate protons; the resulting enolate is stabilized by resonance on its left and right. NaOH is strong enough to remove one of these protons, and then the enolate is methylated at that carbon.



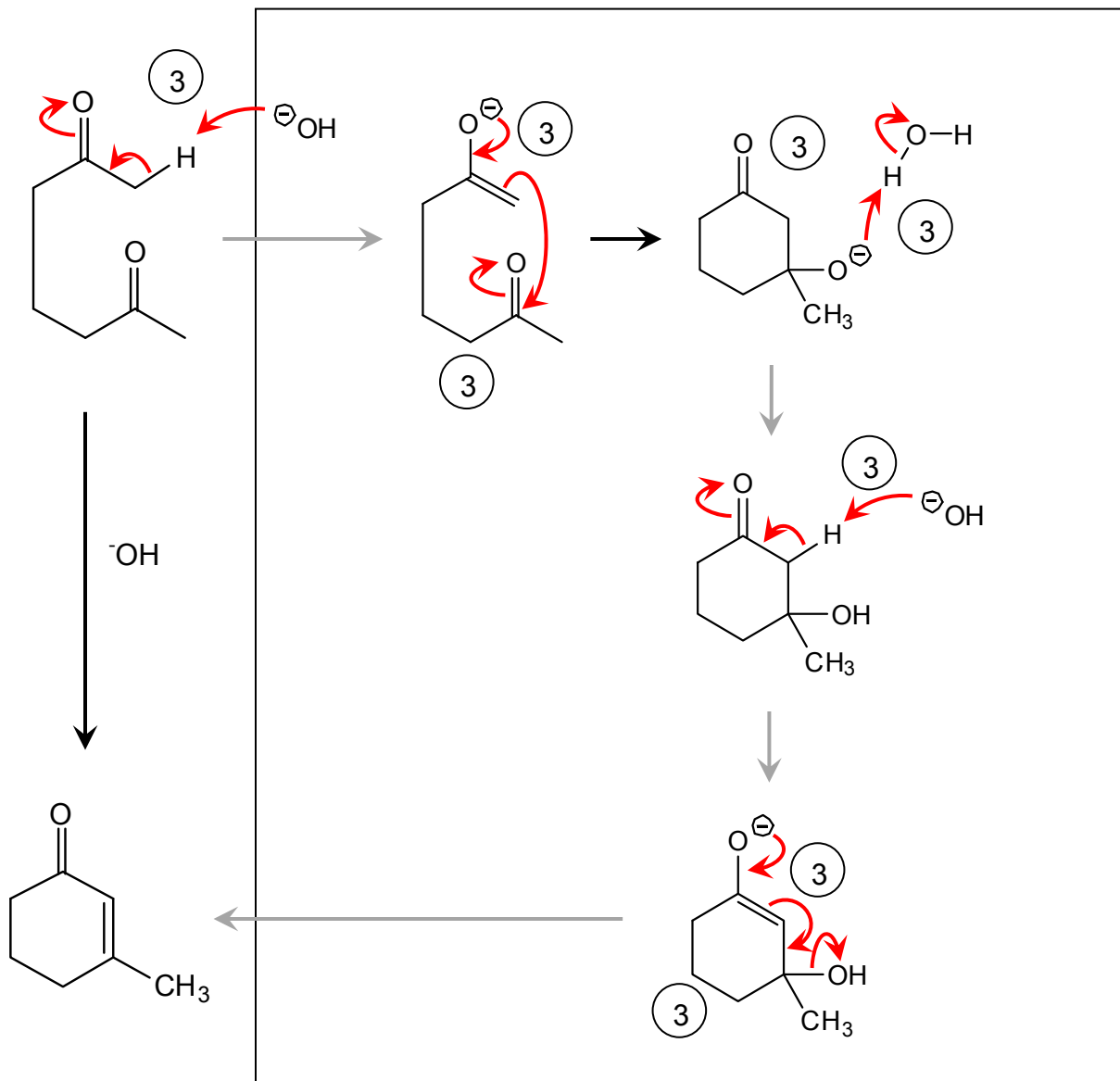
Under these conditions the starting material would be deprotonated to form the kinetic enolate, at the less-substituted carbon. That carbon is then allylated.



4. (24 pts) For the reaction shown below, draw a mechanism that explains how the product is generated from the starting material. In your answer, make sure that you:

- Draw each step of the mechanism separately;
- Use “electron pushing” to show where the electrons in each step go;
- Use only the molecules that you are given; do not invoke reactants or solvents that aren't in the problem.

I have drawn one intermediate in the mechanism for you, but you will still need to push electrons for steps to and from that intermediate.



Rubric:
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. Things that have left for good (e.g., OH^-) and spectators (e.g., H_2O in the middle) may be omitted.

Resonance is NOT a mechanistic step; it is just multiple ways of drawing the same intermediate. As a result, we did not evaluate electron-pushing that showed resonance—you can push electrons for resonance, or not, your choice. In addition, resonance does not have to be shown as an explicit “step”—it can be combined with adjacent steps, for full credit.

3 points for each set of curved arrows shown above in each step. Arrow must start at an electron pair, and end at nucleus where electrons will newly interact.

If you combine steps that can't be combined, you can get points for arrows that are in the rubric, but not for the intermediate you skipped.

Out of these 3 points, 0 points for each use of a generic or incorrect acid/base. You can only use OH^- ; you can't use any other base you may have used in other problems.

3 points for each intermediate structure.

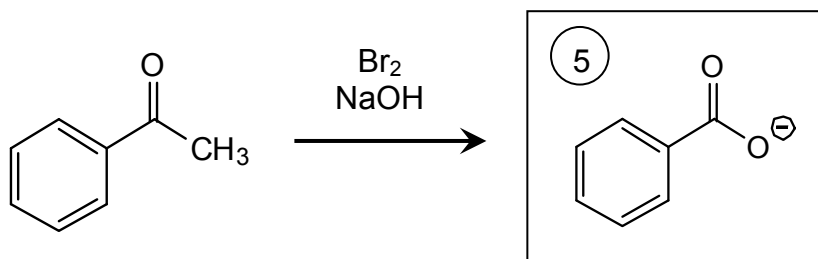
-1 point for each minor error in charge, valency, structure, base, etc.; if error propagates, points are taken off only for initial error.

If you combine steps that can't be combined, you can get points for arrows that are in the rubric, but not for the intermediate you skipped.

Special notes:

-6 points for ending mechanism with an E2 or E1 elimination. The final stage of the reaction is an E1cb reaction.

5. (34 pts) For each of the reactions on the following pages, fill in the empty box corresponding to reactants, reagents, or products. 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”.



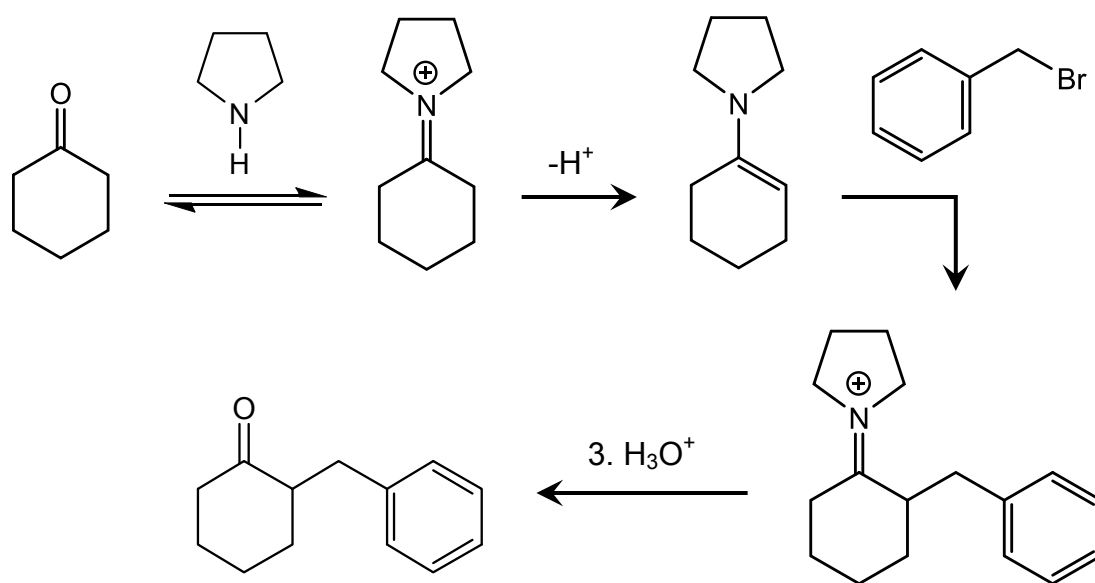
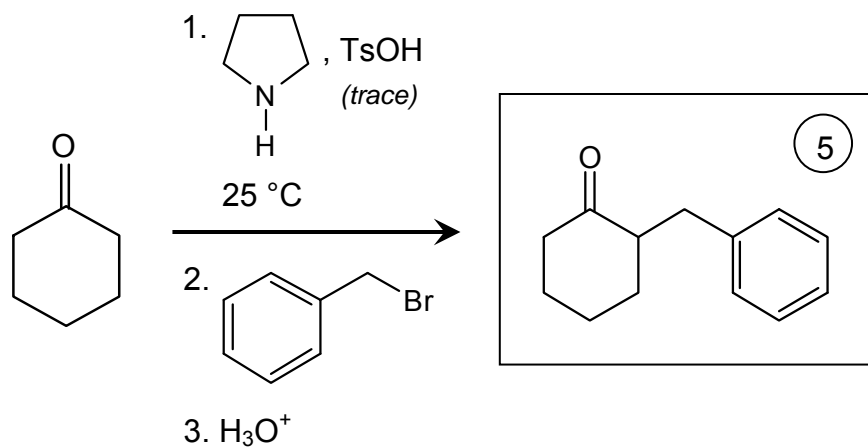
Rubric for this part:

5 points for correct structure.

4 points partial for carboxylic acid (protonated). This would be deprotonated under the basic conditions of the reaction.

2 points partial for trihalomethyl ketone.

1 point partial for any α -halogenated product.

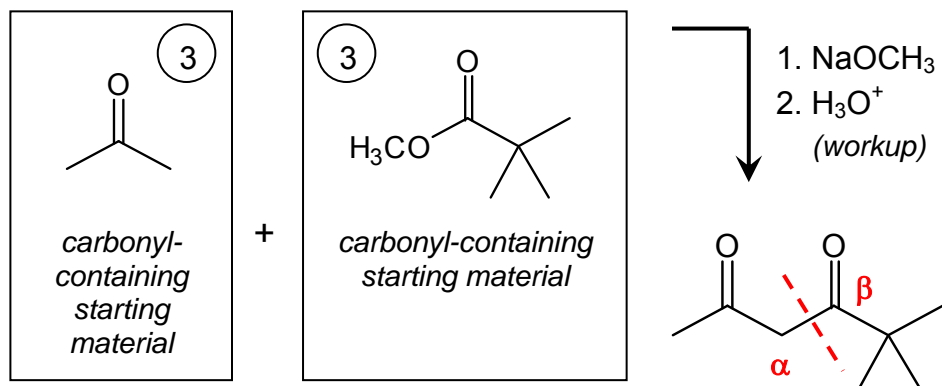


Rubric for this part:

5 points for correct structure.

4 points partial for iminium ion product (that hasn't undergone back-exchange with water).

-2 points for trivial error (like one too many or too few carbons in added group).



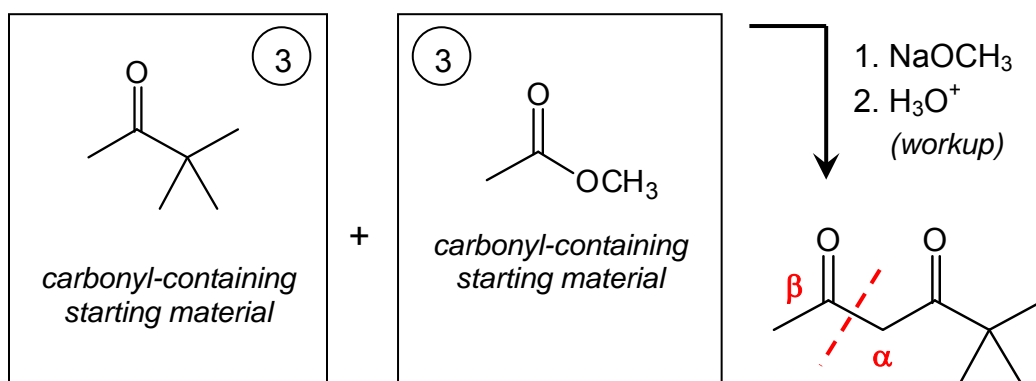
used in excess?

YES or **NO** ?
1

used in excess?

YES or NO ?
1

--OR--



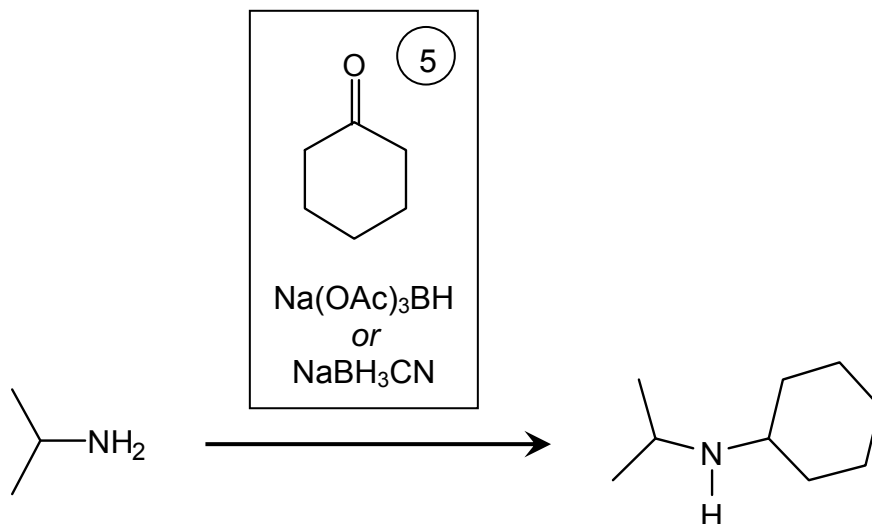
used in excess?

YES or **NO** ?
1

used in excess?

YES or NO ?
1

Both of these sets of answers come from disconnecting the β -diketone product, which is a synthon for the crossed Claisen reaction between a ketone/aldehyde and an ester. Out of those two molecules, the ketone is the most acidic, so it is selectively deprotonated; in order to make the ketone attack the ester selectively, however, the ester needed to be used in excess.



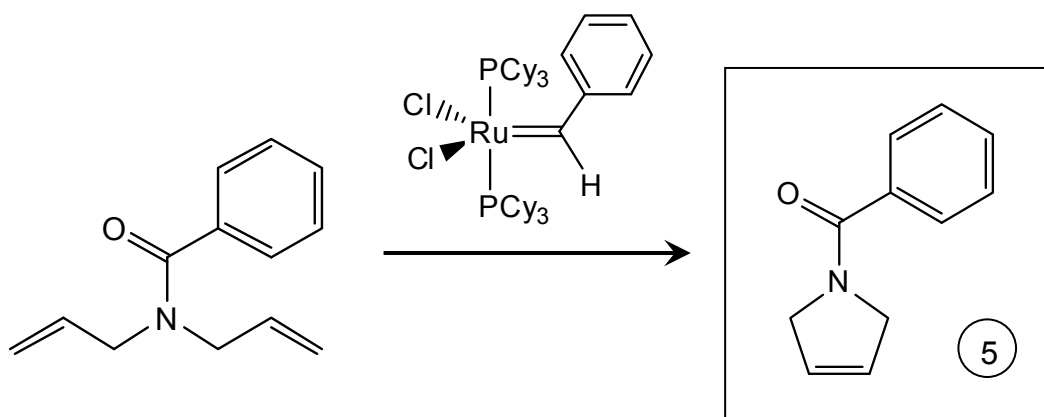
Reductive amination.

Rubric for this part:

5 points for correct structure.

2 points partial for iminium ion (unreduced).

-2 points for trivial error.



Ring-closing metathesis.

Rubric for this part:

5 points for correct structure.

-2 points for trivial error (like one too many or too few carbons in the ring).

