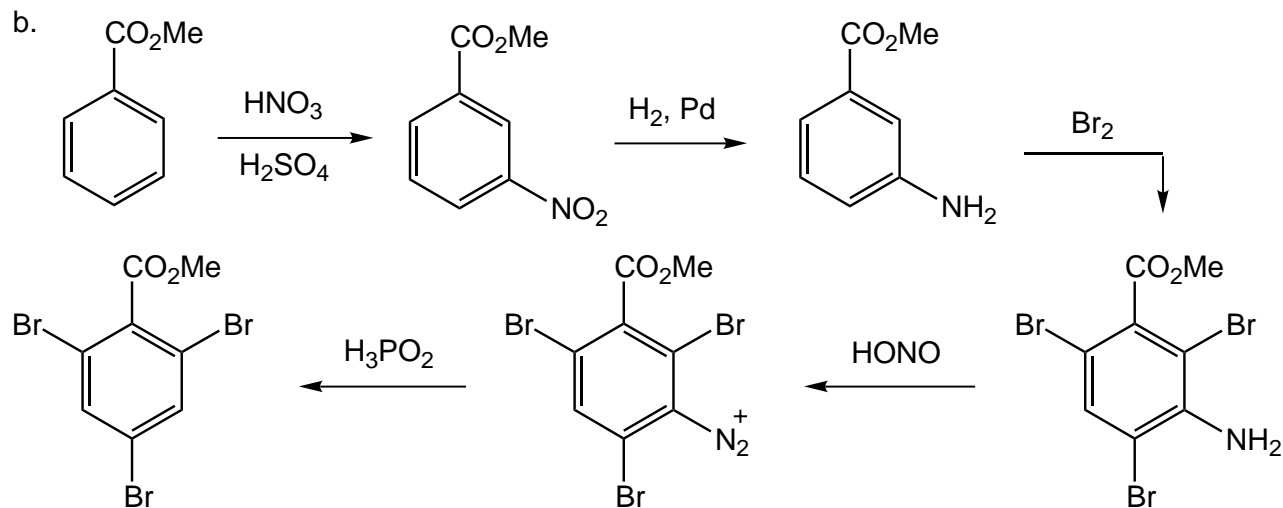
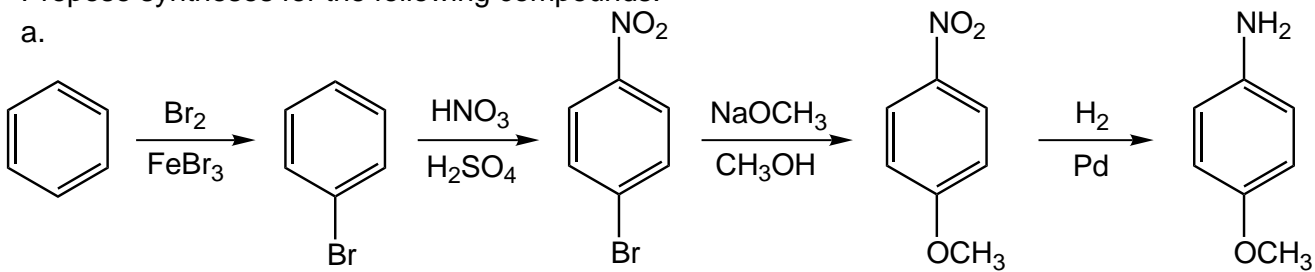


Organic Chemistry c3444y

Problem Set 3 - Nucleophilic Aromatic Substitution, and Aldehydes and Ketones

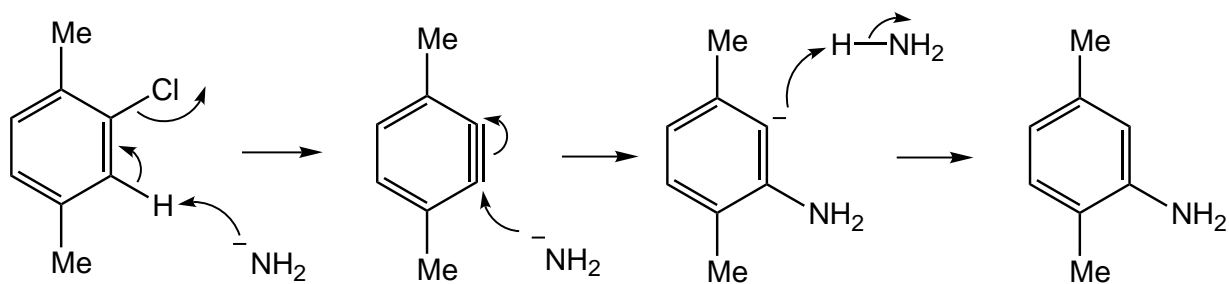
Answer Key

1. Propose syntheses for the following compounds:

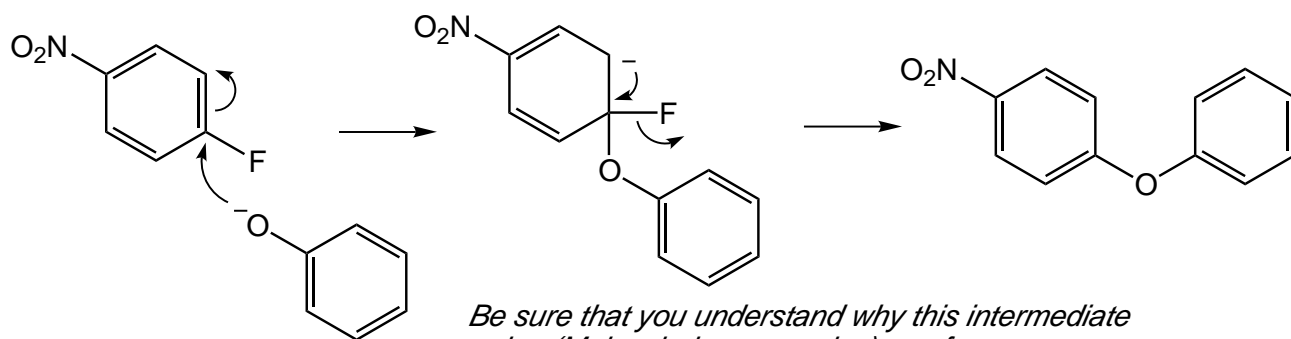


2. Provide detailed mechanisms for the following transformations:

a.

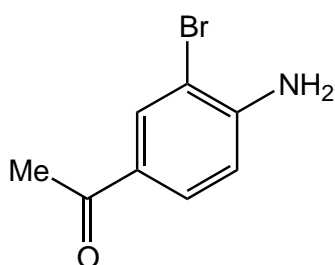
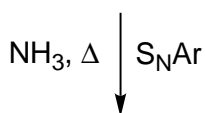
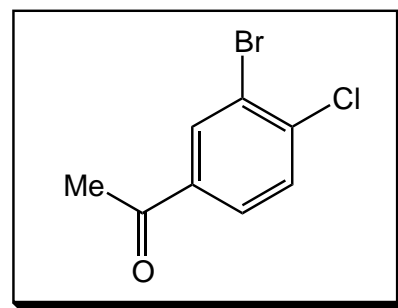
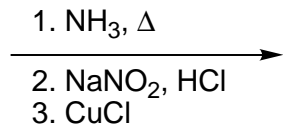
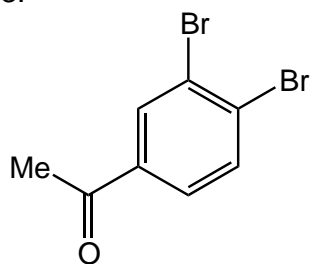


b.

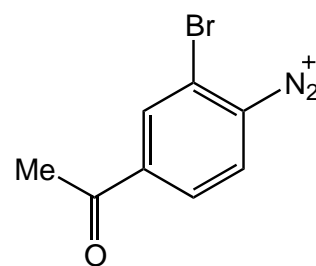
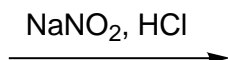


Be sure that you understand why this intermediate anion (Meisenheimer complex) can form.

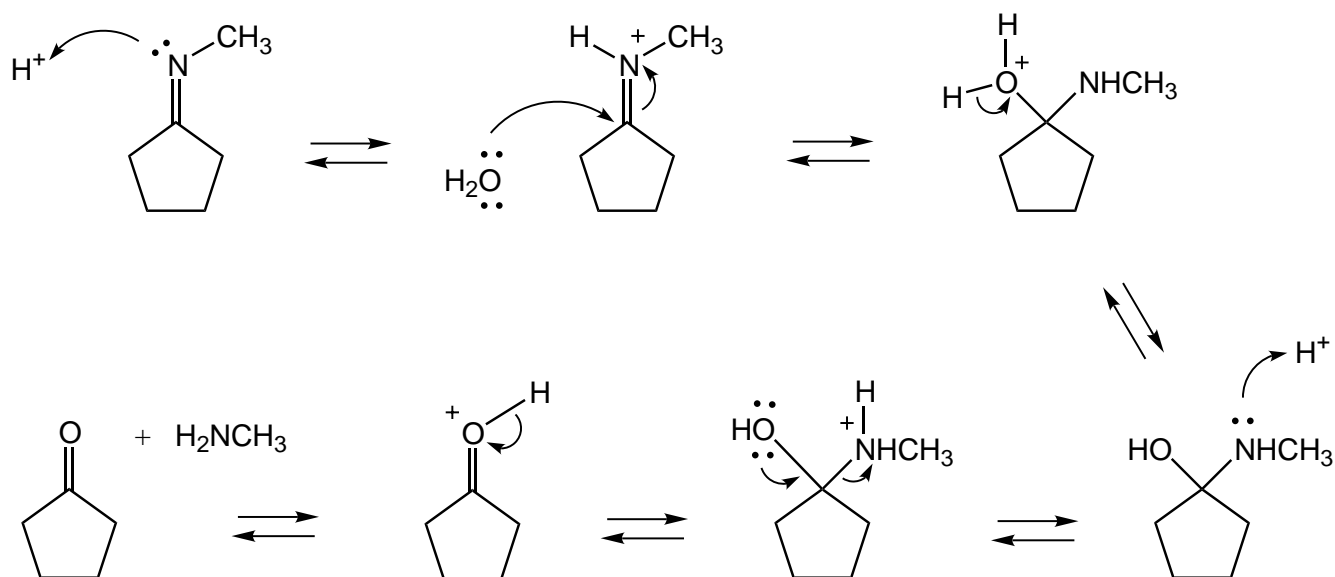
3.



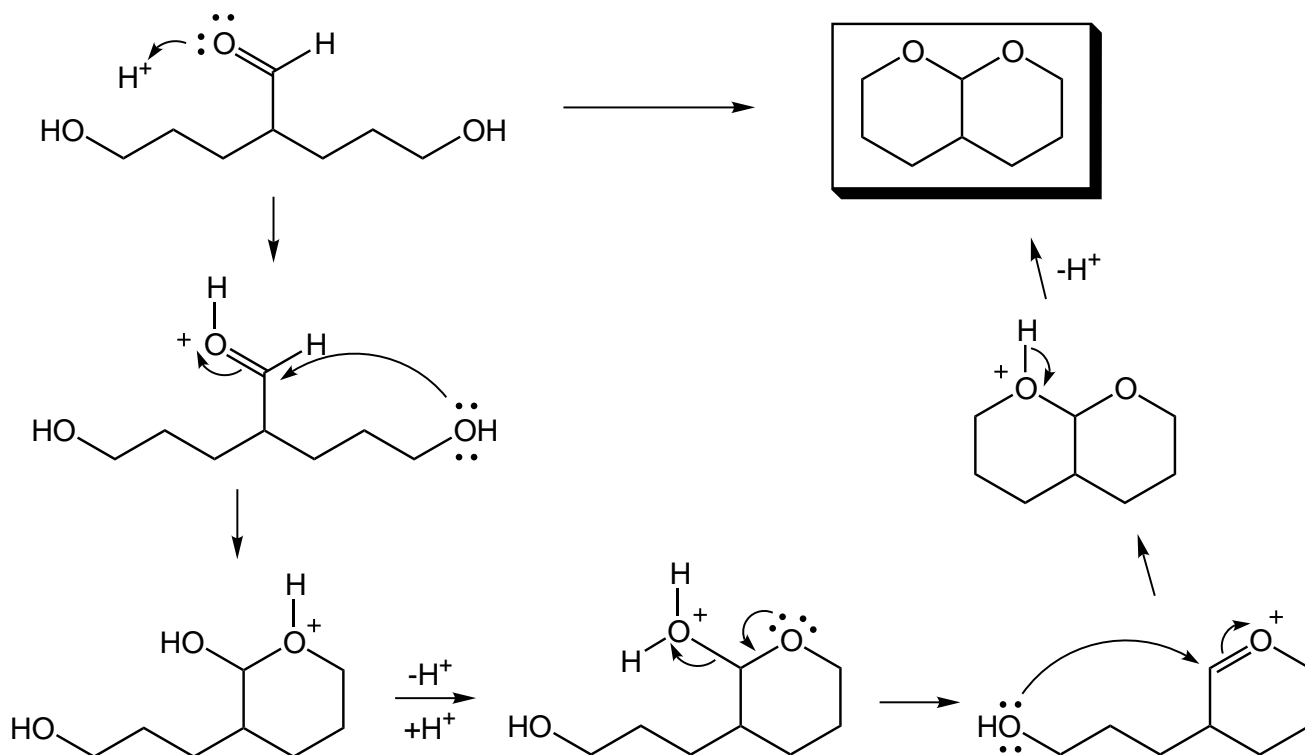
NH_3 is a fairly weak base, certainly too weak to form benzyne. The question then is, is there a properly positioned group to allow $\text{S}_{\text{N}}\text{Ar}$ on one of the bromines? Yes! the ketone can serve as a strong electron-withdrawing group. Draw resonance structures to convince yourself.



4. As we said in class, imine formation is reversible, and the reverse reaction is driven by using an excess of water as well as acid. Write a mechanism for the following transformation:

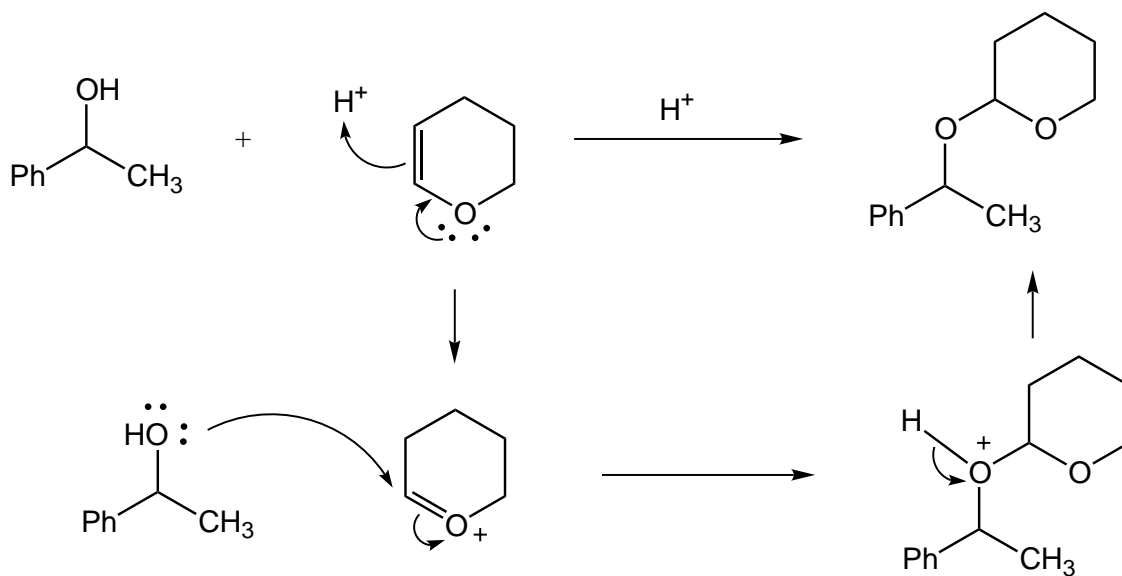


5. Write out a mechanism for, and predict the product of the following reaction:

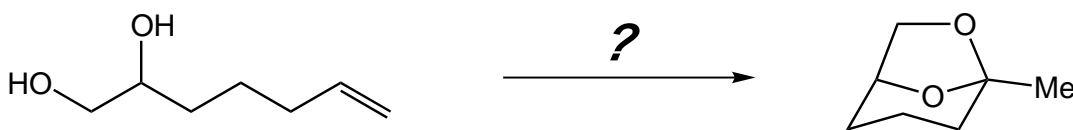


6. Write out a mechanism for the following transformation:

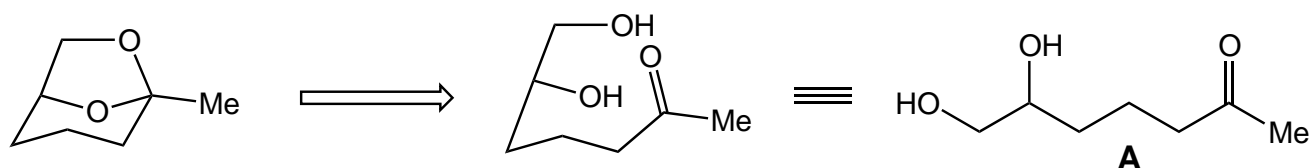
*Hint: You must decide what will happen first with this combination of reagents.
This problem illustrates that there are different ways to make acetals.*



7. Propose a synthesis to achieve the following transformation:
(It should prove helpful to think backwards from the product here. What is the product? How are they made? If you can figure out what is the starting material for the last step, it's relationship to the original starting material should be clearer.)



The product is an acetal (ketal). Acetals are made from an aldehyde or ketone, and two alcohols. Begin by identifying the necessary ketone and alcohols here:



This one operation makes the problem much easier to solve. Now we know that if we can make **A**, then we can simply treat it with acid and get the final product. We're still not done, but the connection between the given starting material and **A** is *much* more obvious.

