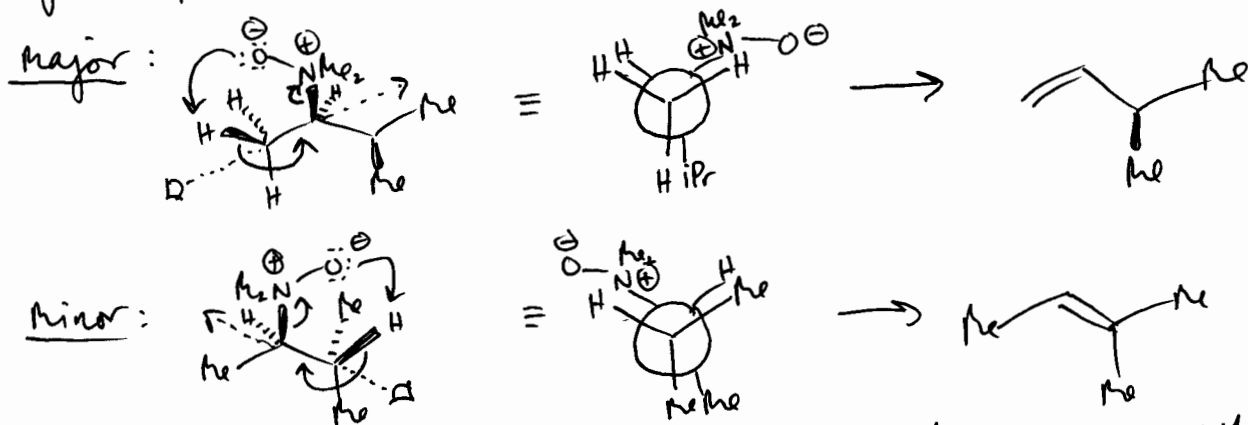
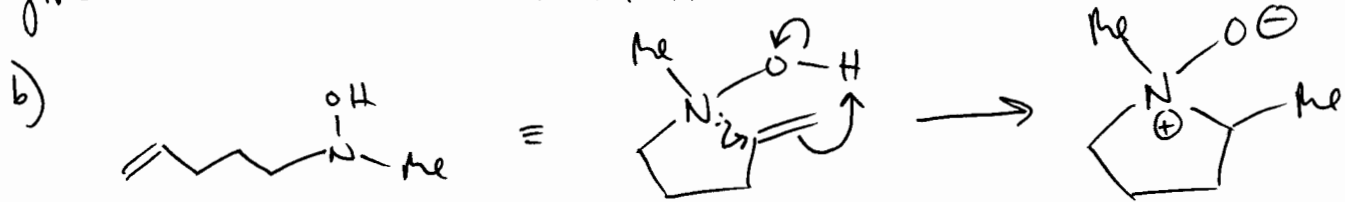


## Problem Set 5 Answer Key

1. a) Compare the energies of the two transition states. Remember, the Cope elimination has to go through a syn-coplanar TS.

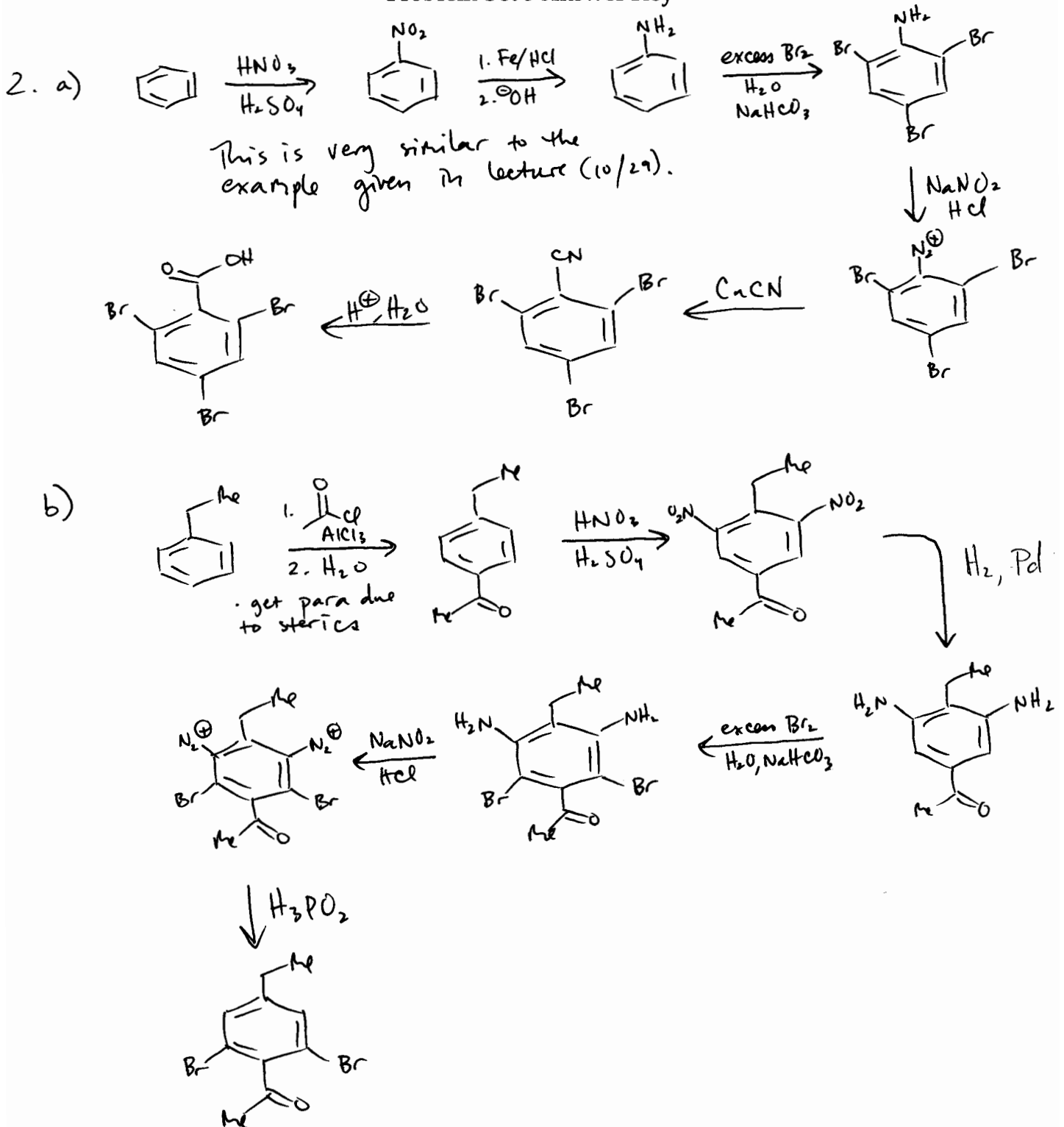


You can ignore the  $\text{H}/\text{NMe}_2\text{O}^\ominus$  interactions since they are in both. In the TS conformer leading to the major product, there is only one additional destabilizing eclipsing interaction ( $\text{H}/\text{iPr}$ ) - not too much worse than  $\text{H}/\text{Me}$ . In the TS conformer leading to the minor product, there are two additional eclipsing interactions ( $\text{H}/\text{Me}$  &  $\text{Me}/\text{Me}$ ). This TS conformer is significantly higher in energy, therefore elimination to give the most-substituted alkene is slower!

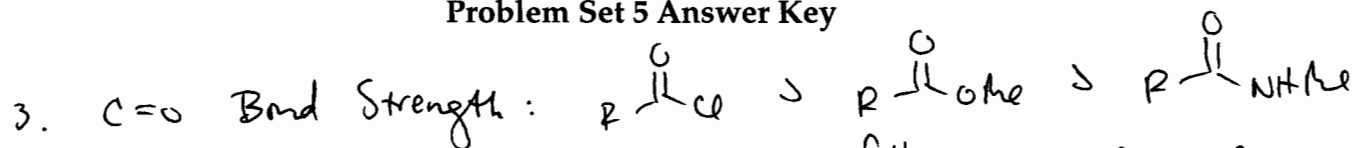


This is the exact opposite of the Cope elimination mechanism. Don't worry about the stereochemistry of the product.

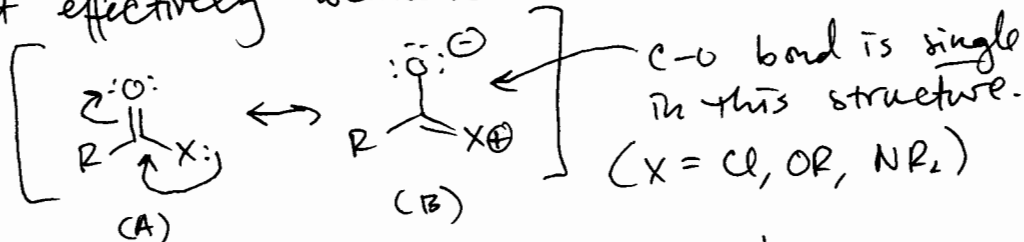
Problem Set 5 Answer Key



Problem Set 5 Answer Key



To explain this trend, think about the following resonance structure (B) that effectively weakens the C=O bond.

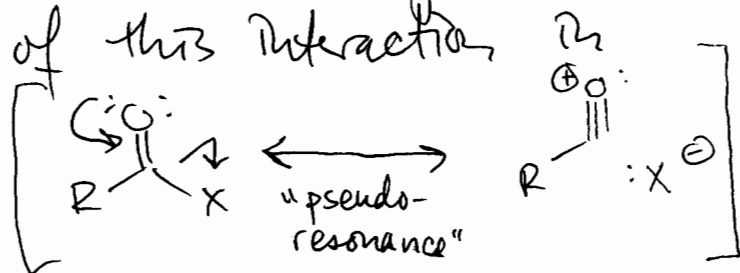


Resonance (B) is very favorable in amides because oxygen is more electronegative than nitrogen. Therefore, the C-O bond order in an amide is somewhere between 1 and 2.

Resonance (B) is less favorable in esters because the electronegative oxygen atom is less effective at donating its electrons and carrying a positive charge. Therefore, the C-O bond order is higher than it is in an amide.

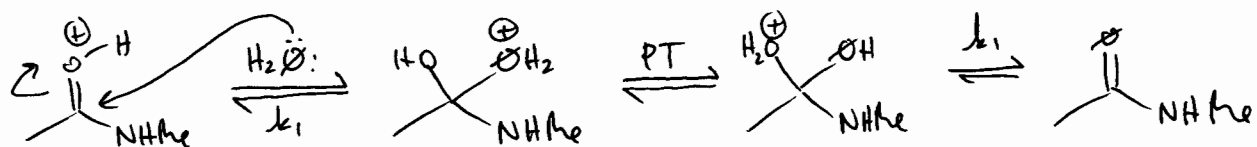
Resonance (B) is very unfavorable in acyl chlorides because Cl is very electronegative and in the row below carbon in the periodic table. Because of this, the chlorine / carbon orbital overlap is very poor, and the C-O bond order is greater than it is w/ the ester.

Advanced: The following orbital interaction also contributes to the trend in bond strengths. Think about the favorability of this interaction in the compounds above.

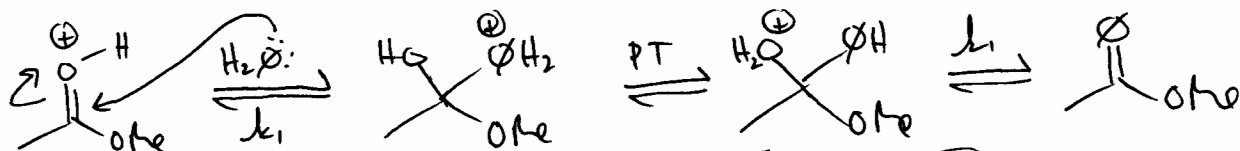
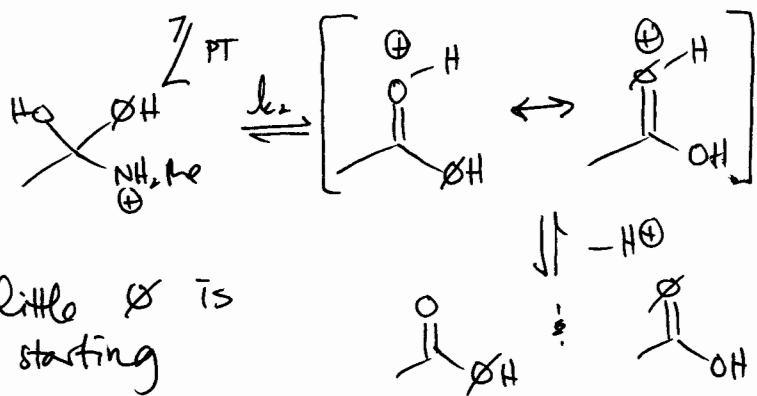


## Problem Set 5 Answer Key

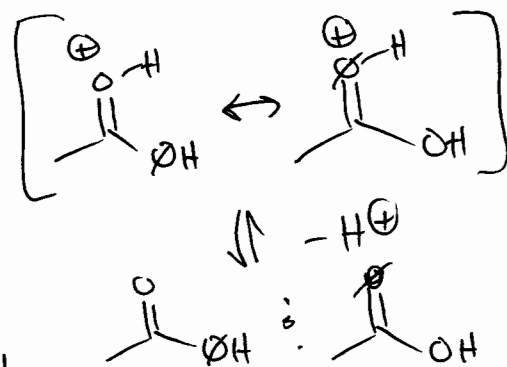
4. Start w/ the mechanisms:



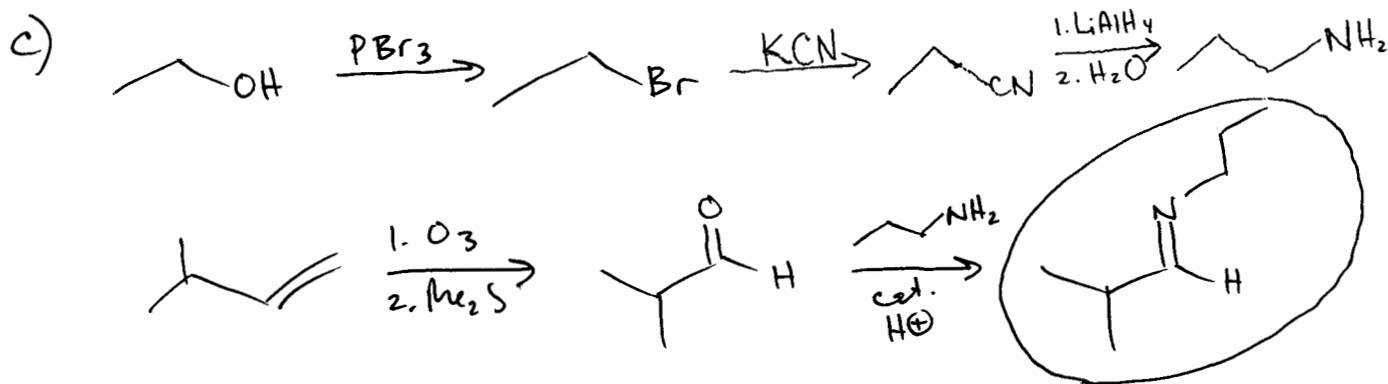
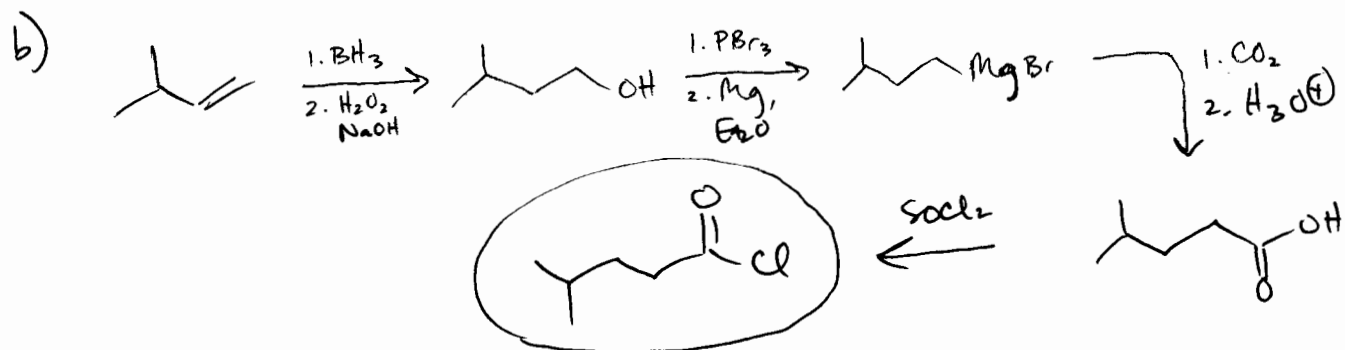
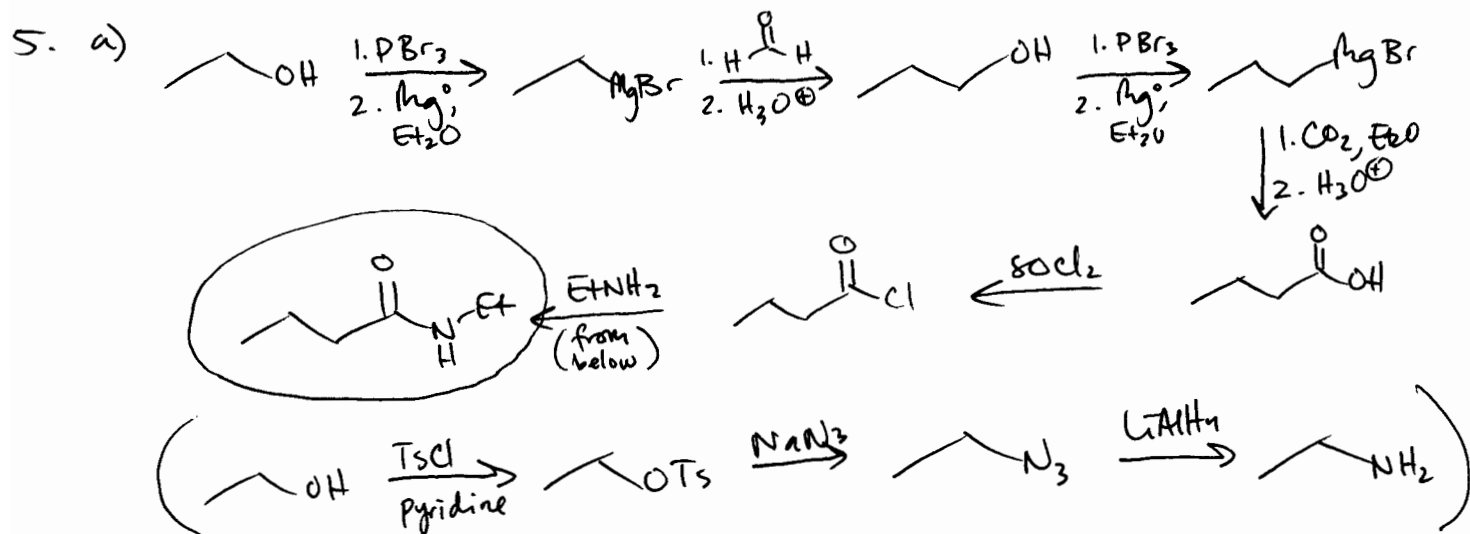
- Proton transfers are very fast.
- Acid/base equilibria favor the protonated N (not O). Therefore, once the tetrahedral intermediate forms, loss of  $\text{NH}_2\text{Me}$  ( $k_2$ ) is faster than loss of  $\text{OHMe}$  ( $k_1$ ); very little  $\phi$  is incorporated into the unreacted starting material.



- All of the oxygens in the tetrahedral intermediate are roughly equally basic. Therefore, each protonated form is present in the same concentration, and  $k_2 \cong k_1$ . As a result, you would expect more  $\phi$  incorporation into the ester starting material than you would into the corresponding amide.



Problem Set 5 Answer Key



Problem Set 5 Answer Key

