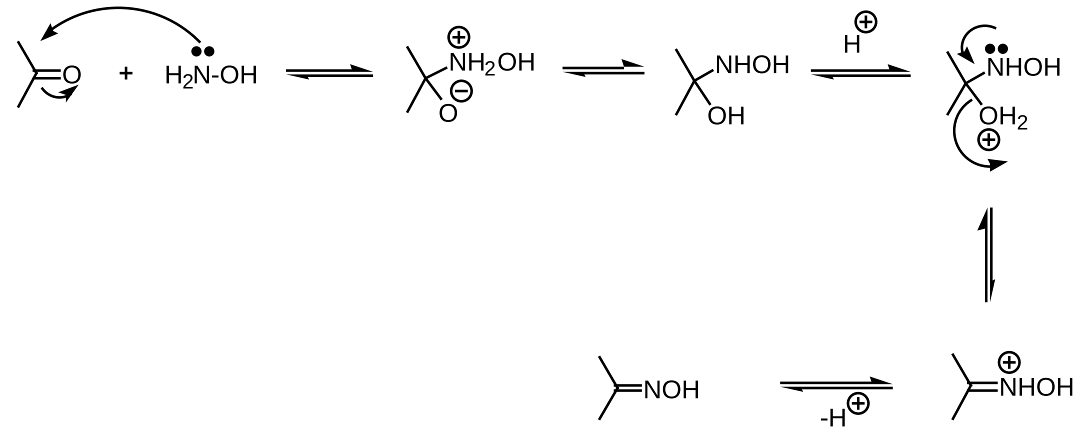
KEY TO Problem set 5.

question 1

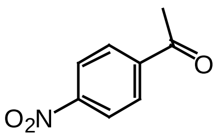
a



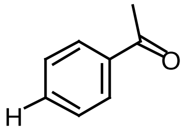
b. At acidic pH (lower then 2) NH_2OH is protonated making it a much weaker nucleophile and therefore reacts much slower.
c. At high pH (above 6) there is very low H^+ concentration the third step (protonation of OH group) is much slower.

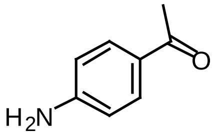
question 2.

IR stretching frequency of the carbonyl is related to the bond strength of the CO. The more single bond character (more contribution of the dipolar form) the weaker the bond and the lower the IR frequency. Therefore the substituent on the aromatic ring that can stabilize the dipolar resonance form (stabilizing the positive charge on carbon) will make the molecule adsorb at the smaller IR frequency.
The order of the stability of the dipolar form is as follows:

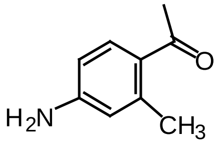


EWG





EDG

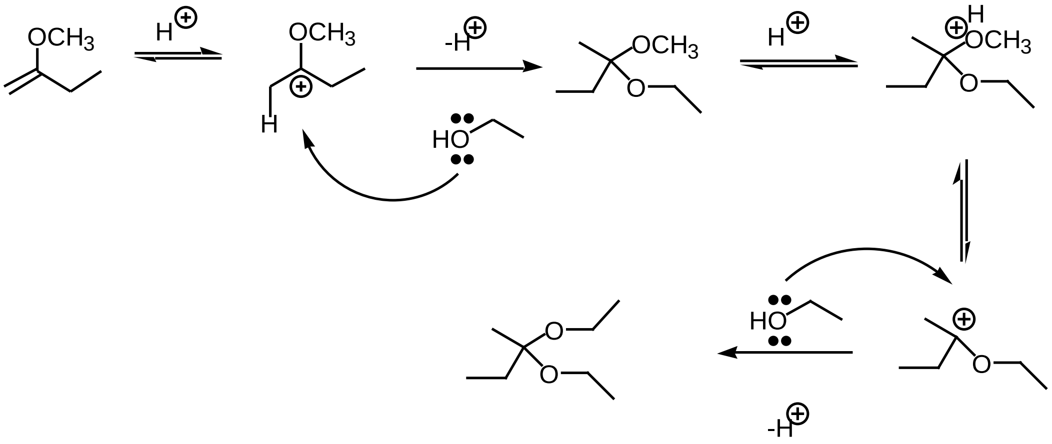


2 EDG

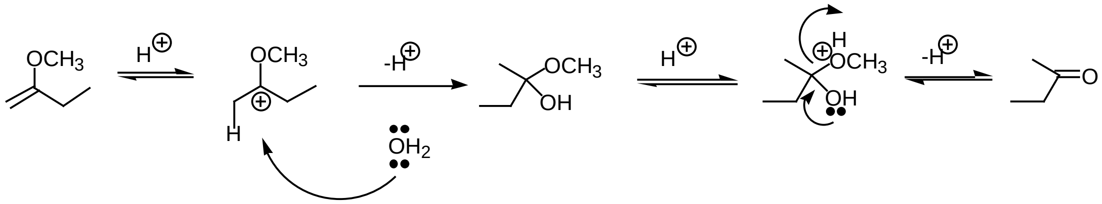
EWG = electron withdrawing group
EDG = electron donating group
And the order of increasing IR frequency is exactly reversed

question 3

A.



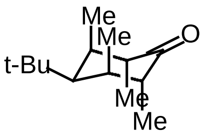
B.



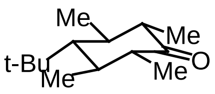
question 4.

CH_3MgBr is a powerful nucleophile that attacks the carbonyl carbon. It can approach the carbon either from the top or from the bottom. The steric environment around the CO should be looked at.

The t-Bu group is prefers to be equatorial and will therefore determine the conformation of the cyclohexane ring.



A

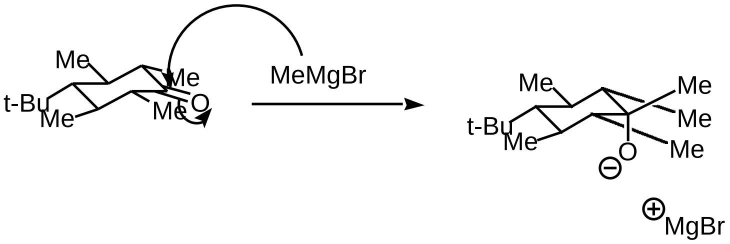


B

In the molecule A the equatorial t-Bu group puts all methyl groups axial thus blocking the top and bottom approach.

In molecule B, however, all methyls are equatorial and both top and bottom attack is possible. Molecule B will therefore react faster.

The mechanism is as follows:


Me
t-Bu
Me
Me
O
Me
MeMgBr
Me
t-Bu
Me
Me
Me
O
Me
⊖
⊕MgBr