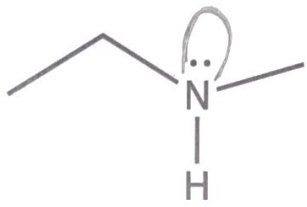
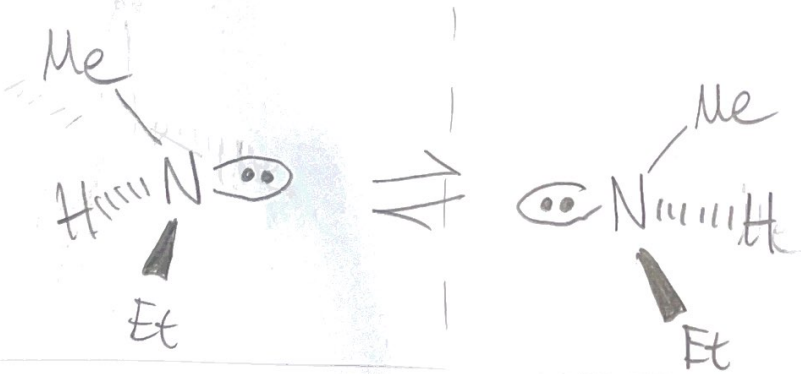
Amines: Rxn Practice and Physical Properties

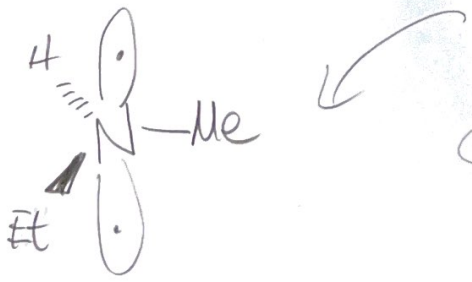
Okay, gang: This worksheet is all about amines. We'll tackle questions regarding some physical properties, acid-base chemistry, and of course, lots and lots of reaction practice. Get your nitrogens ready.

1.) The amine pictured below appears to be a chiral structure. However, the structure below when tested, does not bend the plane of polarized light. Using structure(s) and a brief explanation, account for this lack of chirality in the amine



Dynamic situation: amine inversion continuously happening





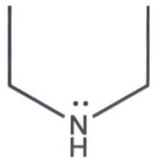
At transition state, molecule is planar, SP_2 hybridized. SP_2 centers are flat, achiral

2.) Let's look at 2 physical properties of amines, and then we'll get into some of the reactions we can use to make amines and reactions we can do with amines.

a.) Given the four molecules below, rank them from 1-4 in regards to strength of intermolecular forces, 4 being the molecule with the strongest intermolecular forces. (Hint: remember what we talked about regarding Hydrogen Bonds)

3

3 H-Bond locations

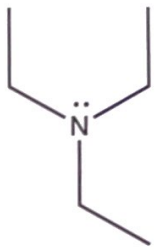


2

2 H-Bond locations

4

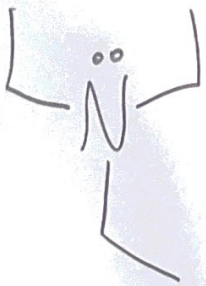
3 H-Bond locations (Stronger due to electronegativity of oxygen)



1

NO H-Bond locations

b.) Of the above molecules, one **cannot** donate a Hydrogen Bond at all: Identify which molecule it is as well as explain why this is the case.

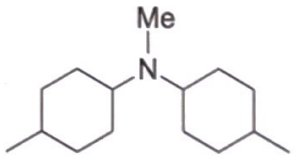


There is no N-H covalent bond present, so no hydrogen bonding can occur

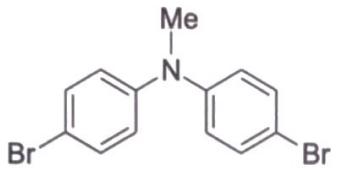
More basic structure is where N has strongest δ- charge

c.) Given the 4 molecules below, rank them from 1 – 4, 1 being the **weakest** base and 4 being the **strongest** base. After ranking, justify your choice for 1, the weakest base (with a short explanation or structures).

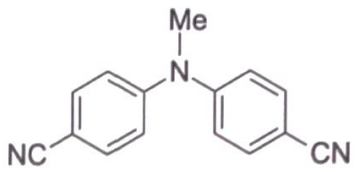
- Resonance decreases negativity of N
- EWGs further decrease negativity



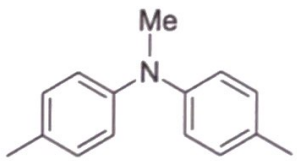
4



2

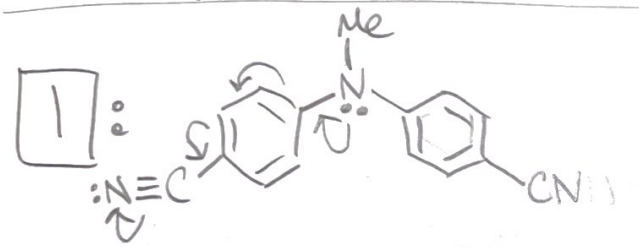


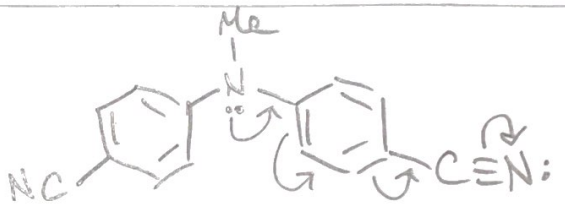
1



3

1:





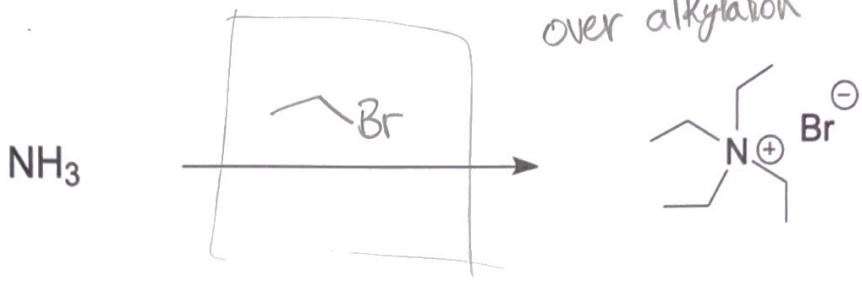
*Resonance with both aromatic rings + EWG greatly decreases negativity of N, making it the weakest base

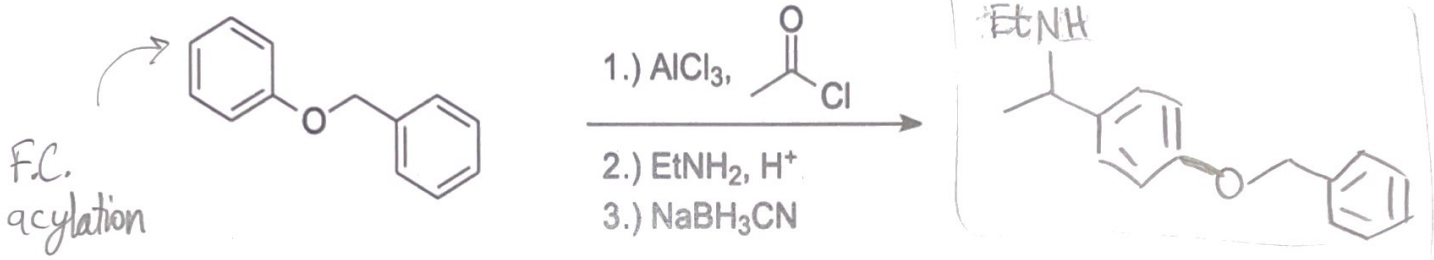
2: 2 & 3 have resonance that put a negative charge on the

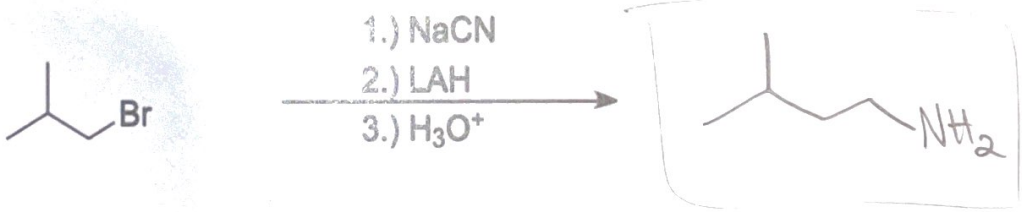
3: central N, but halogens deactivate benzene rings and don't donate e⁻ better than the methyl groups do.

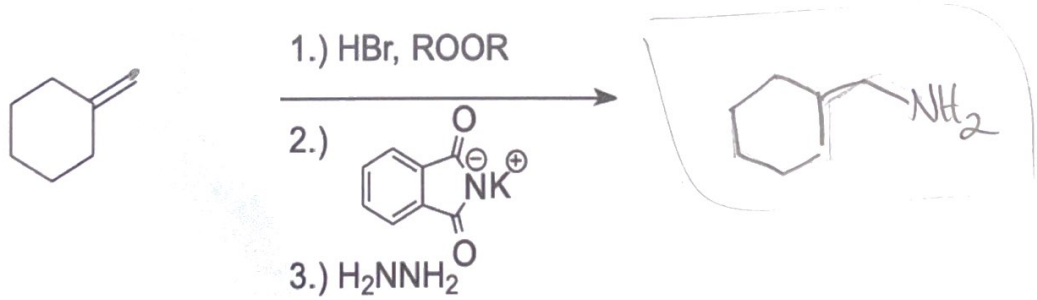
4: No resonance is present; therefore the partial negativity of the N is strongest here ultimately leading to the strongest basic character

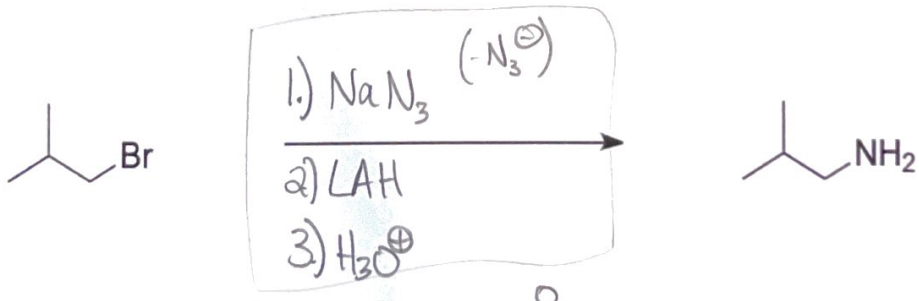
3.) Alright gang, let's head into some complete the reaction/provide the reagent/provide the reactant problems. We're going to tackle everything from creating amines via S_N2 to the Mannich reaction—you got this.



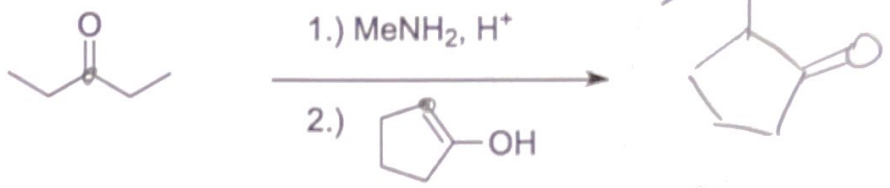




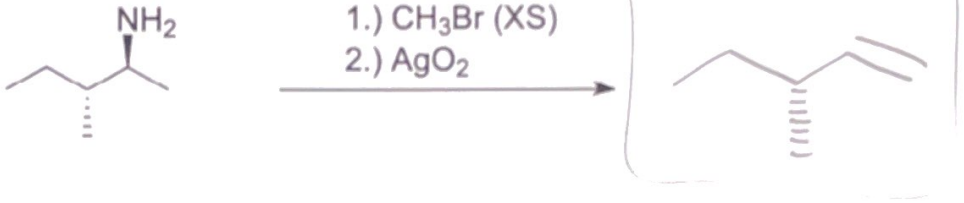


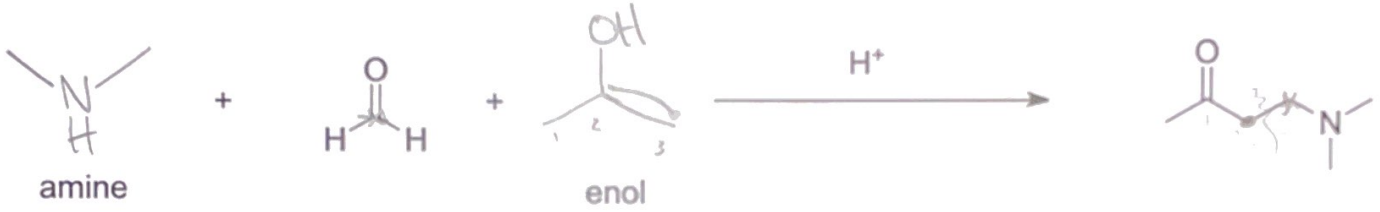


Mannich Rxn



Hofmann Elim



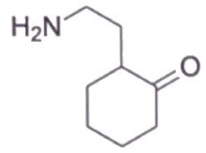


Mannich

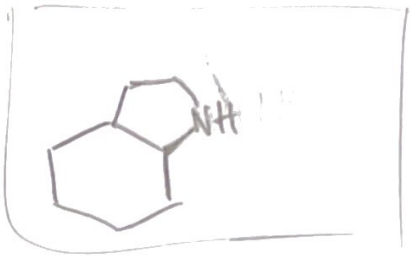
Reduce Amination, intramolecular

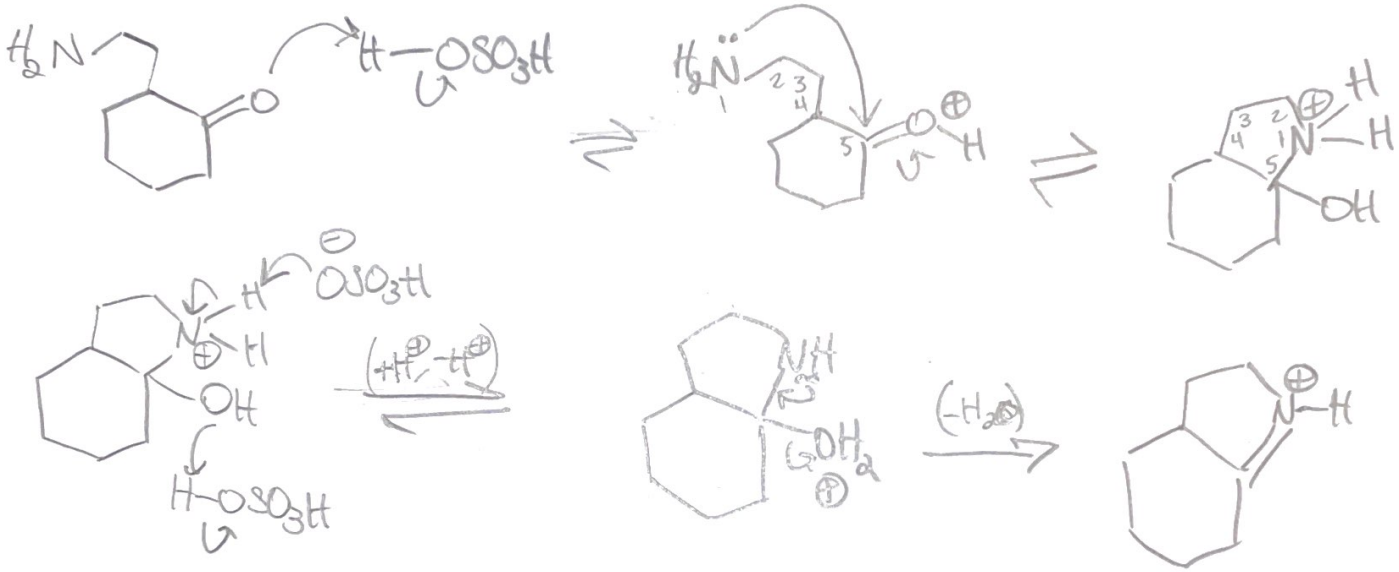
4.) And to finish this worksheet out, we have a complete the reaction + mechanism problem. Predict the product for the reductive amination reaction, and draw the arrow pushing mechanism.

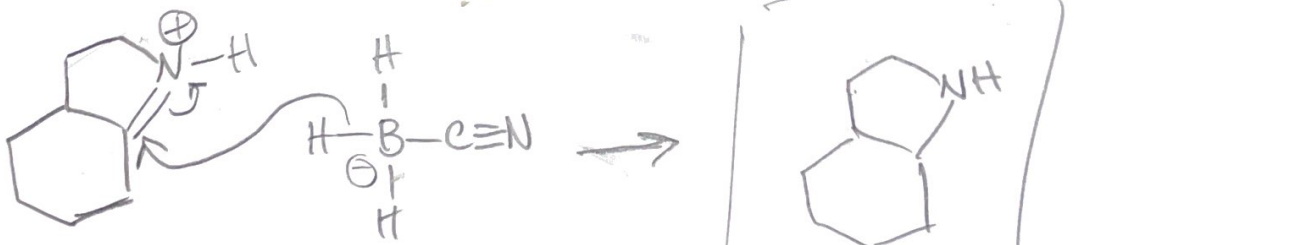
① Imine formation
② Reduction w/ mild source of $H:^{\ominus}$



1.) H_2SO_4
2.) $NaBH_3CN$







or use $H:^{\ominus}$ instead of drawing $BH_3CN^{\ominus}$