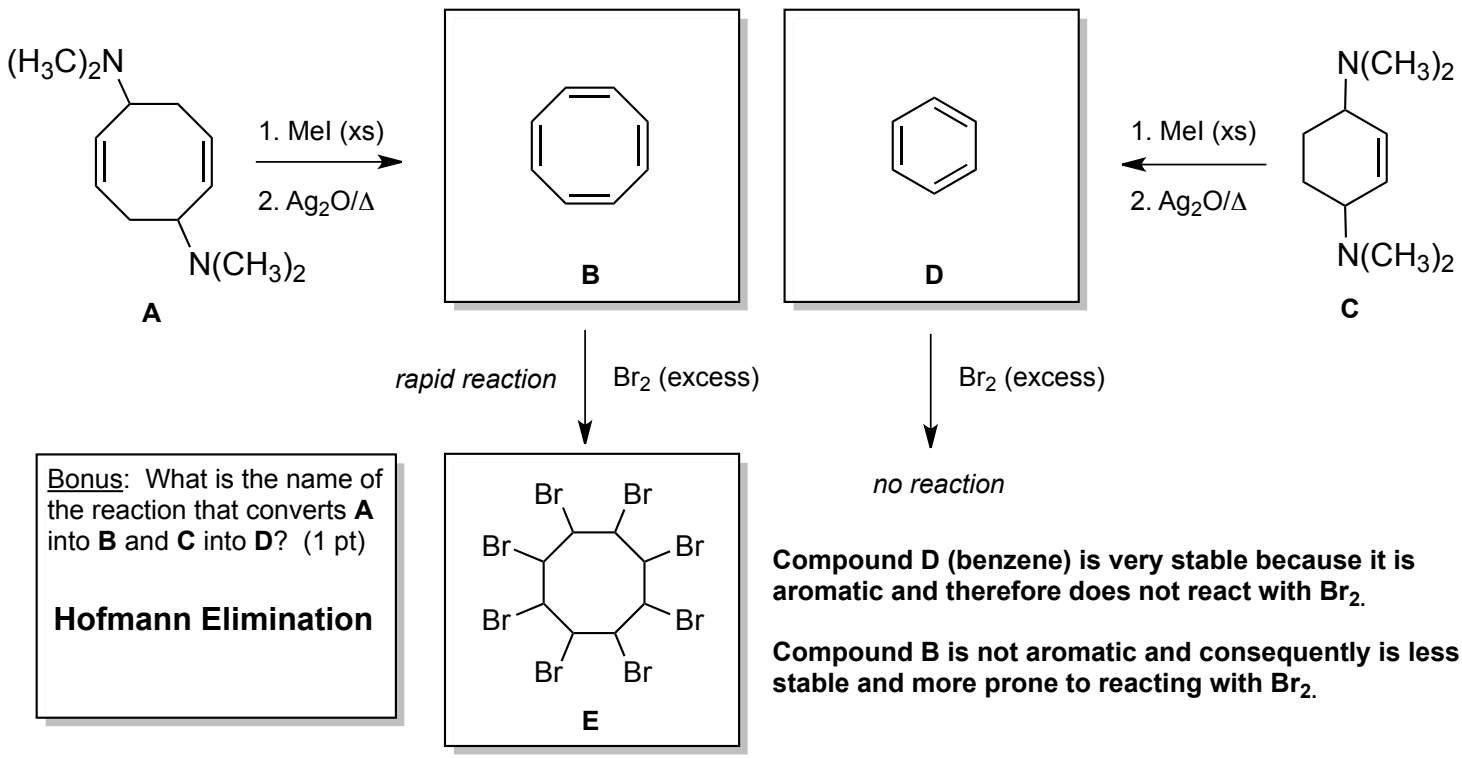
Chemistry 41c
THIRD QUIZ KEY
May 17, 2013

Name (print)_____Answer Key_____

Note: You have 55 minutes to take the quiz. This exercise is to be worked alone and is closed book and closed notes. No electronic devices are allowed.

Why do you think they call it dope?

1. Richard Willstatter (1915 Chemistry Nobel Laureate) treated diamine **A** with excess methyl iodide, and then with excess Ag_2O and heat, whereupon a hydrocarbon **B**, C_8H_8, distilled from the reaction mixture. Compound **B** rapidly reacted with excess Br_2 under mild conditions. Treatment of compound **C** in the same way gave a hydrocarbon **D**, C_6H_6, which did not react with excess Br_2. Identify compounds **B**, **D,** and **E** and in a sentence or two explain the different reactivity of **B** and **D** towards Br_2 (Willstatter concluded from these experiments that compound **D** could not be an alkene). (6 pts)



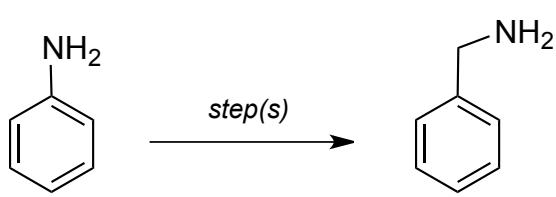
Bonus: What is the name of the reaction that converts **A** into **B** and **C** into **D**? (1 pt)

Hofmann Elimination

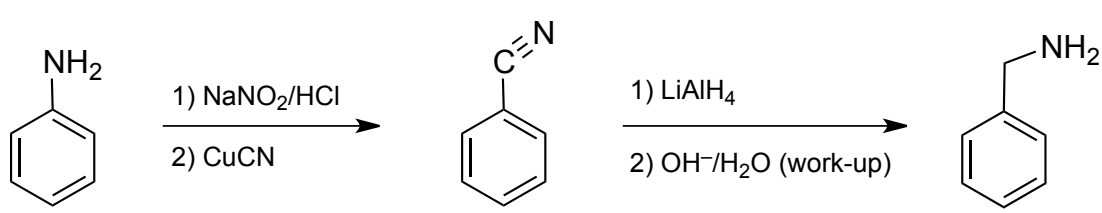
Compound D (benzene) is very stable because it is aromatic and therefore does not react with Br_2.

Compound B is not aromatic and consequently is less stable and more prone to reacting with Br_2.

2. Outline a sequence of reactions that would bring about the conversion of aniline into benzylamine. (4 pts)



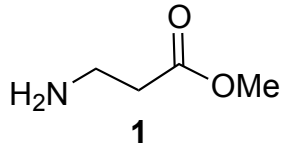
aniline benzylamine



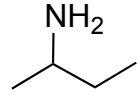
H_2, cat. were also accepted for this step

3. Arrange the amines within each set in order of increasing basicity in aqueous solution, least basic first. Indicate your answers by placing the compound numbers in the boxes for each series.

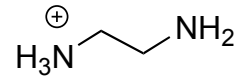
(a)



1



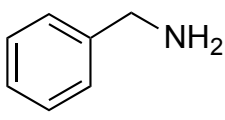
2



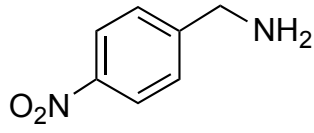
3

least basic [**3**] < [**1**] < [**2**] *most basic* (3 pts)

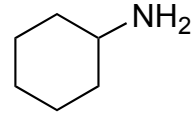
(b)



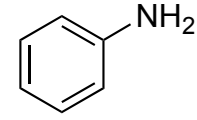
1



2



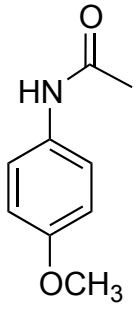
3



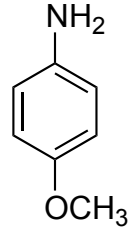
4

least basic [**4**] < [**2**] < [**1**] < [**3**] *most basic* (4 pts)

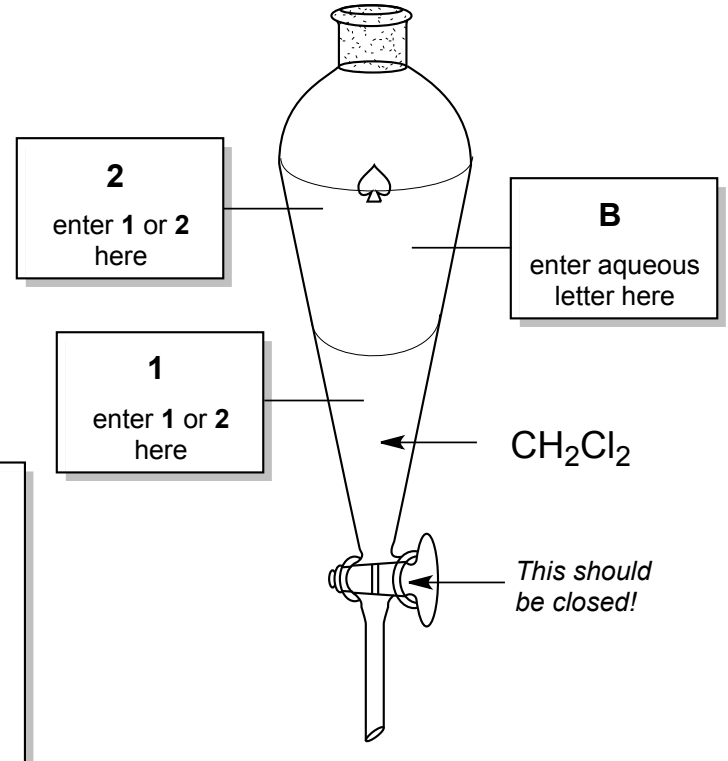
4. You are asked to use an extractive procedure to separate *p*-methoxyacetanilide (**1**) from *p*-methoxyaniline (**2**). Devise a dichloromethane-aqueous protocol by selecting the appropriate aqueous solution (**A**, **B**, **C**, or **D**) and then identify the location of compounds **1** and **2** in the biphasic system within the separatory funnel. Mark your answers in the boxes provided. (3 pts)



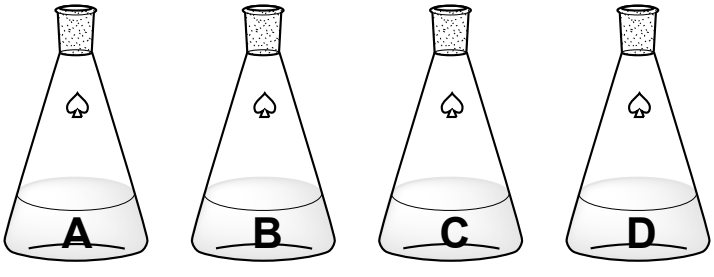
1



2



Select one of these aqueous solutions:



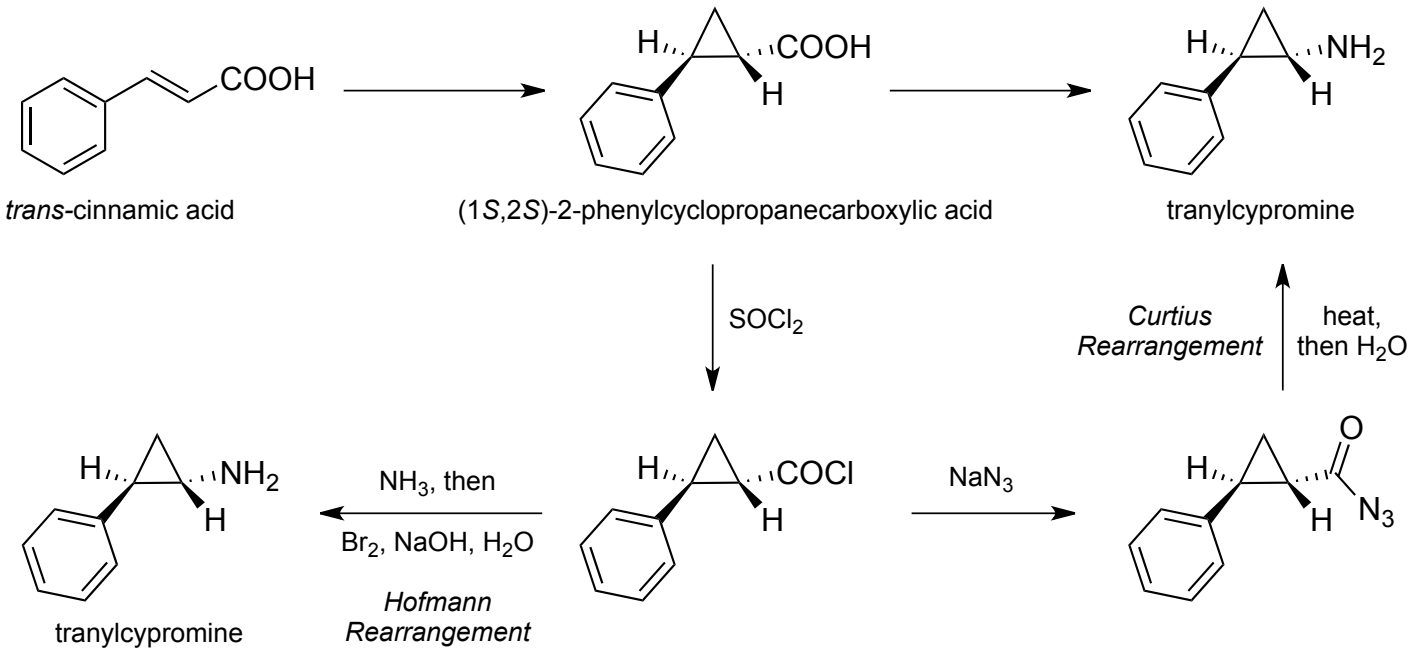
5% NaOH pH 14	5% HCl pH -0.8	5% $NaHCO_3$ pH 8.0	25% NaCl pH 7.2

Bonus: Once you have separated **1** from **2**, how would you retrieve the compound in the aqueous layer? (2 pts)

Treat the aqueous layer with base, then extract with organic solvent and collect the organic layer.

5. The antidepressant drug tranylcypromine is a primary amine with the amino group on a cyclopropane ring. Show how you would convert an enantiomer of 2-phenylcyclopropanecarboxylic acid (which is made from *trans*-cinnamic acid) to tranylcypromine. (*Hint:* If someone is asking you to rearrange your atoms, it is best to be courteous.) (4 pts)

Bonus: What reaction would you use to effect the first transformation shown below? (2 pts) **Simmons–Smith reaction**



6. Alizarin yellow R is an azo dye that changes color from yellow to red between pH 10.2 and 12.2. Outline a synthesis of alizarin yellow R from aniline, salicylic acid (*o*-hydroxybenzoic acid), and any other reagents. (6 pts)