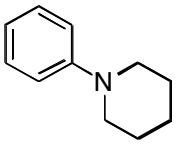
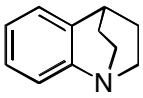
Problem Set #5
Due: November 3, 2006, 12:00 PM

1. Explain the fact that the amines shown below have considerably different basicities despite obvious similarities in structure.

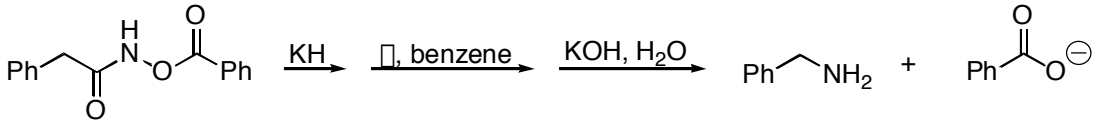
	A	B	C
			
pK_a NH^+	**5.20**	**7.79**	**10.95**

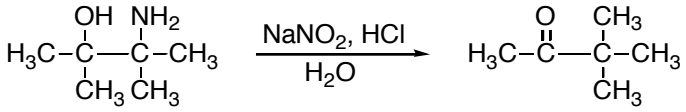
2. Give the organic product(s) expected when *p*-chloroaniline reacts with:
a) dilute HBr
b) C_2H_5MgBr
c) $NaNO_2$, HCl, 0^oC
d) *p*-toluenesulfonyl chloride

3. Give the organic product(s) expected when the product of #2c reacts with:
a) H_3O^+/H_2O
b) CuBr
c) H_3PO_2
d) CuCN

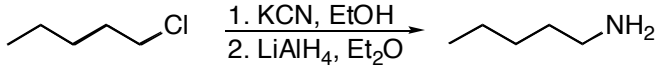
4. Explain the following observation. The diazotization of 2,4-cyclopentadien-1-amine give a diazonium salt, which, unlike most aliphatic diazonium ions, is relatively stable and does not decompose to a carbocation.

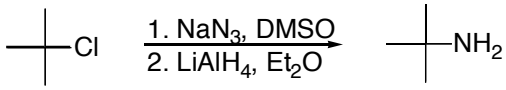
5. Provide a mechanism for each for the following transformations.

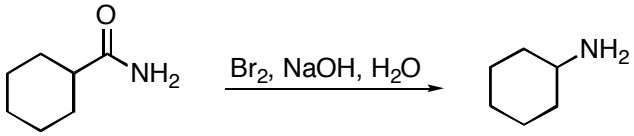


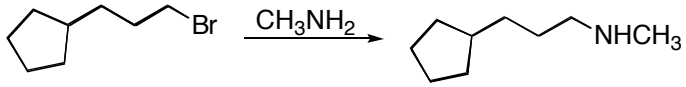


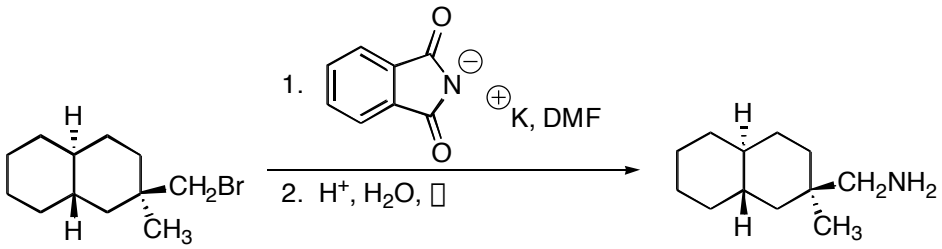
6. The following syntheses are proposed for the following amines. In each case, indicate whether the synthesis will work well, poorly, or not at all. If a synthesis will not work well, explain why.

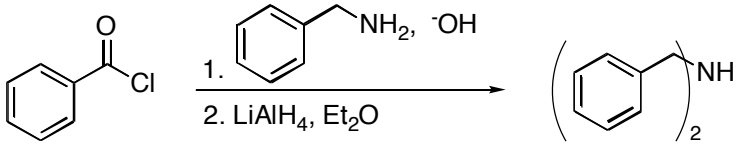
a) 

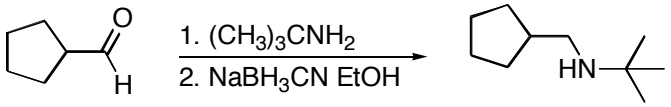
b) 

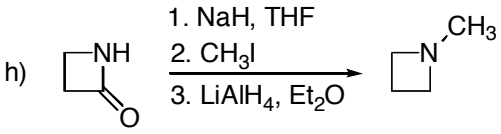
c) 

d) 

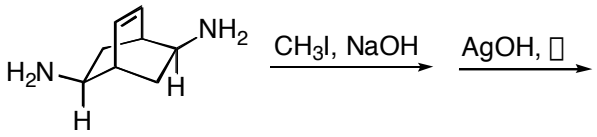
e) 

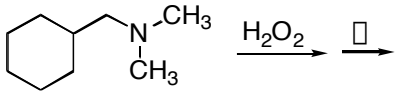
f) 

g) 

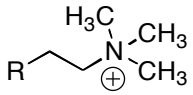
h) 

7. Provide a mechanism and product(s) for each of the following reactions.

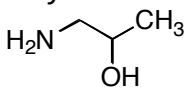


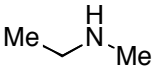
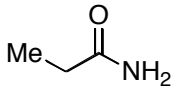


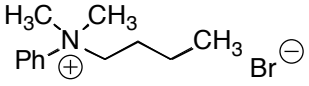
8. Rank the following compounds in terms of increasing rate of Hofmann elimination (1 = slowest reaction).



R = $(CH_3)_3C$
R = H
R = H_3C

9. Outline a synthesis for each of the following compounds.
a) ethylamine from methanol
b) ethylamine from ethanol
c)  from ethanol

d)  from 

e) benzylamine from aniline
f)  from butyraldehyde

g) *m*-chlorobromobenzene from nitrobenzene
h) *p*-chlorobromobenzene from nitrobenzene