CHEM 256 – Phillips – April 28, 2008

**Test 4 – Version 1**

By signing below, I certify that I have neither given nor received any unauthorized help on this exam, and have followed good test-taking practices

Student Name: _____

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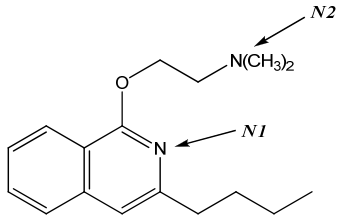
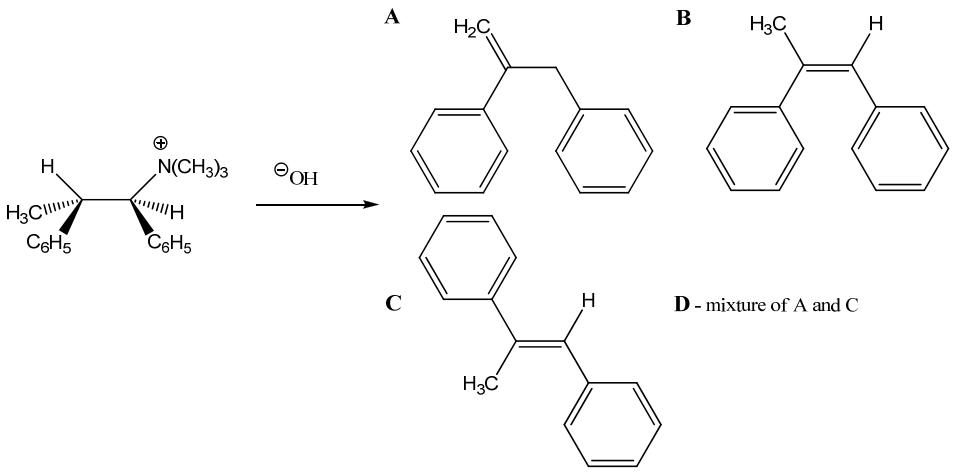
1. Which nitrogen (***N1*** or ***N2***) in the following compound is more basic and why? [homework problem 25.49 c.] Choose the true statement.




dimethisoquin
(local anesthetic)

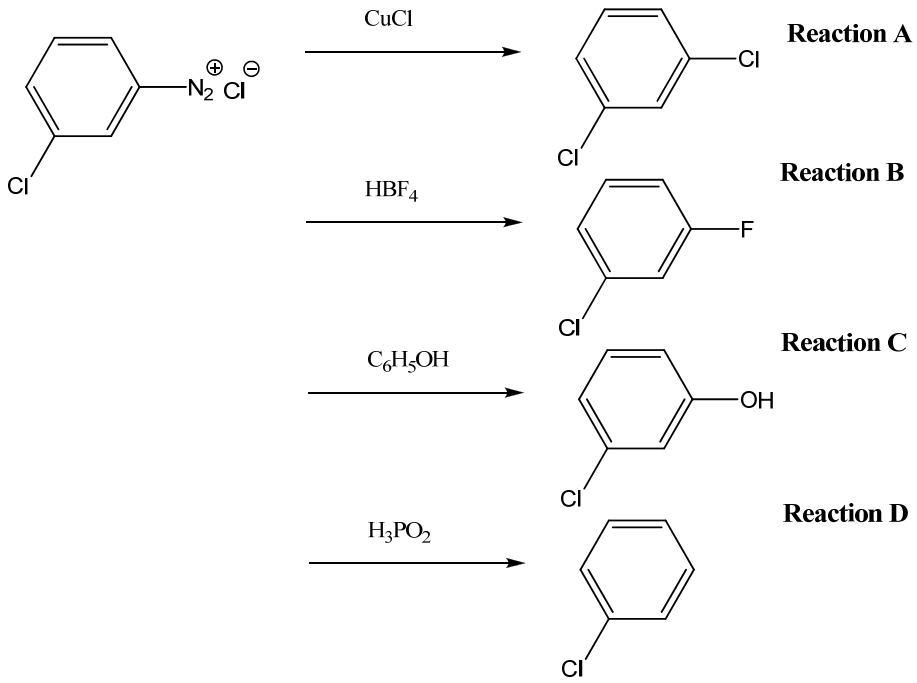
   A. The $sp^2$ ***N1*** is more basic because of hybridization effects, increasing the s character of a bond increases its acidity
   B. The $sp^3$ ***N2*** is less basic due to the electron donating power of substituent alkyl groups
   C. The $sp^3$ ***N2*** is more basic due to hybridization effects (less s character) and the electron donating power of alkyl substituents
   D. Both ***N1*** and ***N2*** are of comparable base strength

2. What is the correct stereochemistry of the alkene(s) formed from the Hofmann elimination of the following quaternary ammonium salt? [homework problem 25.65 b.]




   A. A
   B. B
   C. C
   D. mixture of A and C

3. In Chapter 25, we learned a long list of reagents which react with diazonium salts to prepare other structures. Which reaction of those listed will not lead to the product indicated? [homework problem 25.66]

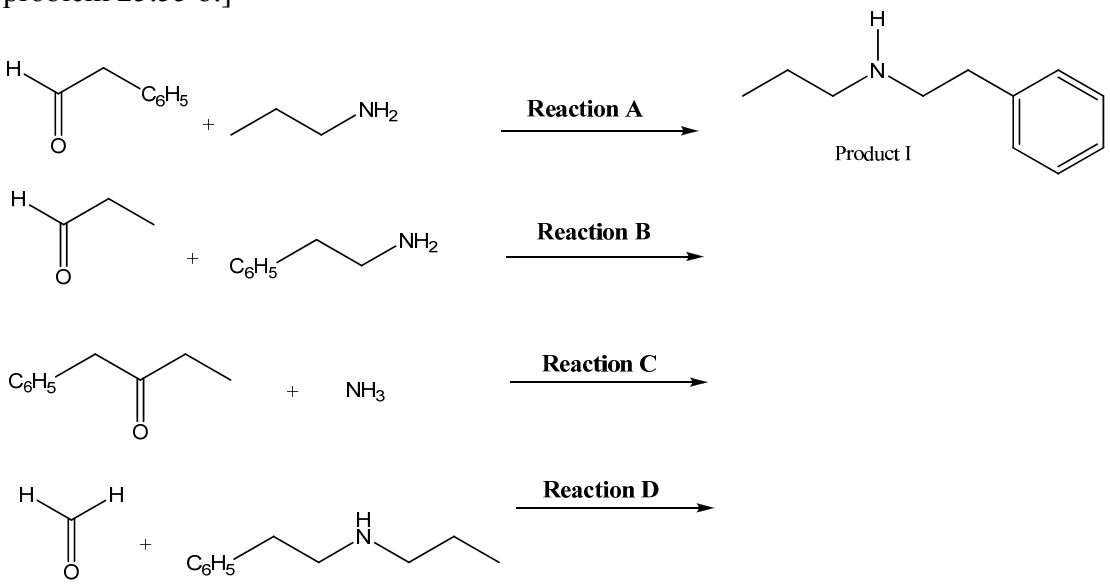



A. Reaction A
B. Reaction B
C. Reaction C
D. Reaction D
E. All are correct

4. An amine with three different substituents is a stereogenic center, so why do we not have to worry about there being two enantiomers? [Chapter 25 practice test, question #1]

A. There must be four bonds to have a chiral center.
B. There is rapid inversion at nitrogen, so the two forms interconvert.
C. Enantiomers only occur at carbon.
D. It isn't an alkene.

5. Which of the following reactions between the carbonyl and nitrogen compounds listed will produce Product I using a reductive amination reaction, as shown? [homework problem 25.55 b.]

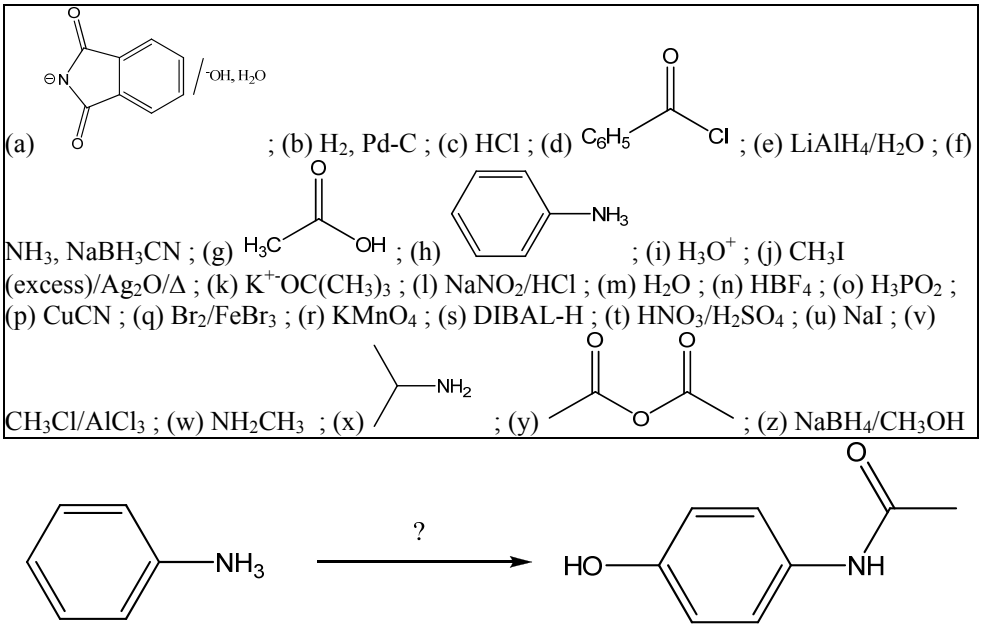



A. Reaction A
B. Reaction B
C. Reaction C
D. Reaction D
E. Both Reaction A and Reaction B

6. Why is direct nucleophilic substitution a poor method for preparing secondary and tertiary amines from primary amines? [Chapter 25 practice test, question #7]

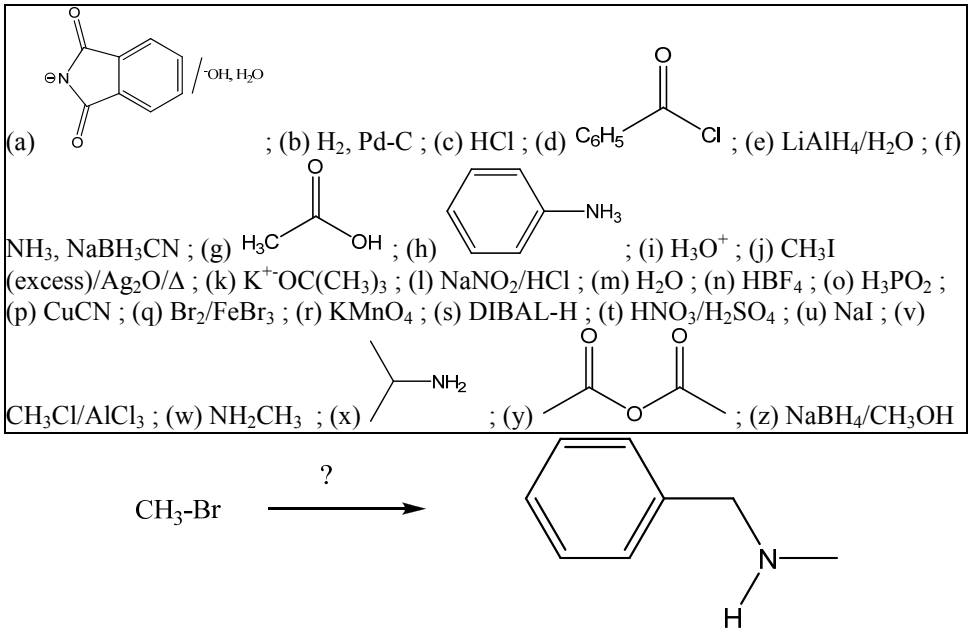
A. A primary amine is not a nucleophile.
B. A primary amine is too hindered.
C. Since the product is a nucleophile, it can continue to be alkylated (i.e., overalkylation).
D. A large excess of the alkyl halide is required.

7. Choose the best reagents from the list provided to complete the following synthetic transformation(s). [Synthesis question #1]



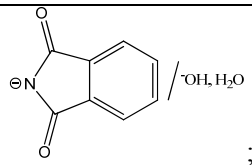
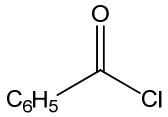
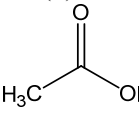
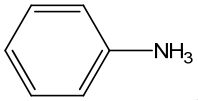
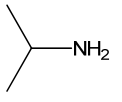
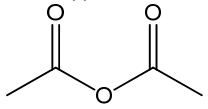

A. (v), (r), (y)
B. (y), (v), (r)
C. (l), (m), (t), (b), (y)
D. (l), (o), (t), (b), (g)

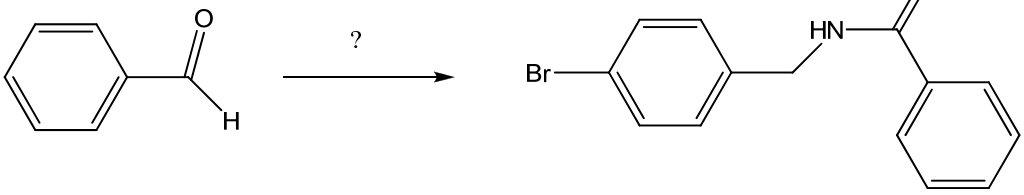
8. Choose the best reagents from the list provided to complete the following synthetic transformation(s). [Synthesis question #2]




A. (w), (j), (d)
B. (a), (d), (z)
C. (w), (y), (z)
D. (a), (d), (e)

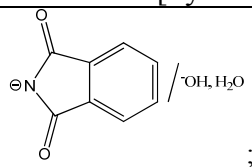
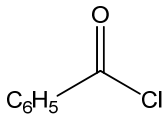
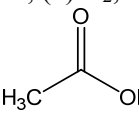
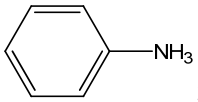
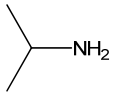
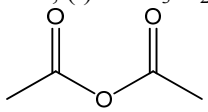
9. Choose the best reagents from the list provided to complete the following synthetic transformation(s). [Synthesis question #3]

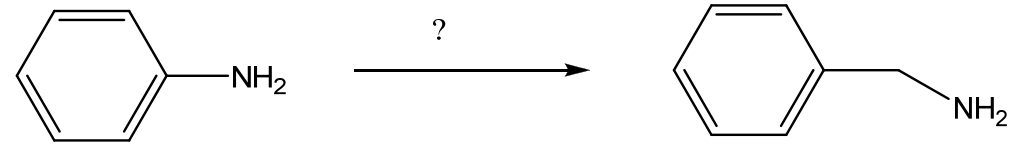
(a)  ; (b) $H_2$, Pd-C ; (c) HCl ; (d)  ; (e) $LiAlH_4/H_2O$ ; (f) $NH_3$, $NaBH_3CN$ ; (g)  ; (h)  ; (i) $H_3O^+$ ; (j) $CH_3I$ (excess)/$Ag_2O/\Delta$ ; (k) $K^+{}^-OC(CH_3)_3$ ; (l) $NaNO_2$/HCl ; (m) $H_2O$ ; (n) $HBF_4$ ; (o) $H_3PO_2$ ; (p) CuCN ; (q) $Br_2/FeBr_3$ ; (r) $KMnO_4$ ; (s) DIBAL-H ; (t) $HNO_3/H_2SO_4$ ; (u) NaI ; (v) $CH_3Cl/AlCl_3$ ; (w) $NH_2CH_3$ ; (x)  ; (y)  ; (z) $NaBH_4/CH_3OH$



A. (f), (q), (d)
B. (q), (f), (d)
C. (w), (d)
D. (z), (d), (f)

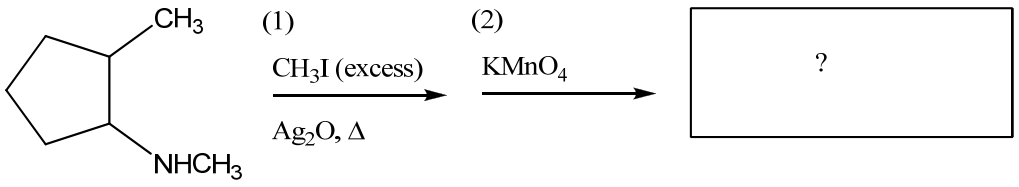
10. Choose the best reagents from the list provided to complete the following synthetic transformations. [Synthesis question #4]

(a)  ; (b) $H_2$, Pd-C ; (c) HCl ; (d)  ; (e) $LiAlH_4/H_2O$ ; (f) $NH_3$, $NaBH_3CN$ ; (g)  ; (h)  ; (i) $H_3O^+$ ; (j) $CH_3I$ (excess)/$Ag_2O/\Delta$ ; (k) $K^+{}^-OC(CH_3)_3$ ; (l) $NaNO_2$/HCl ; (m) $H_2O$ ; (n) $HBF_4$ ; (o) $H_3PO_2$ ; (p) CuCN ; (q) $Br_2/FeBr_3$ ; (r) $KMnO_4$ ; (s) DIBAL-H ; (t) $HNO_3/H_2SO_4$ ; (u) NaI ; (v) $CH_3Cl/AlCl_3$ ; (w) $NH_2CH_3$ ; (x)  ; (y)  ; (z) $NaBH_4/CH_3OH$

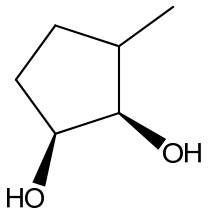


A. (y), (e)
B. (l), (p), (e)
C. (j), (k)
D. (l), (n), (w)

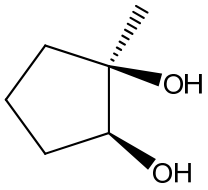
11. Choose the correct structure for the product produced in the following series of reactions.



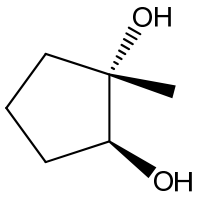

A.



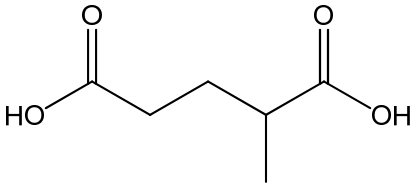

B.




C.

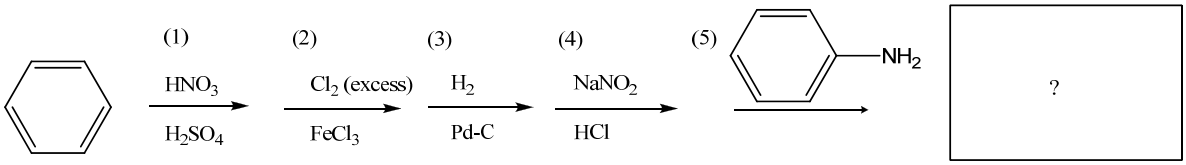



D.

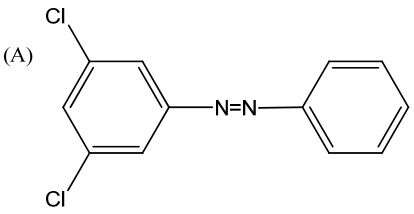



E. mixture of B and C

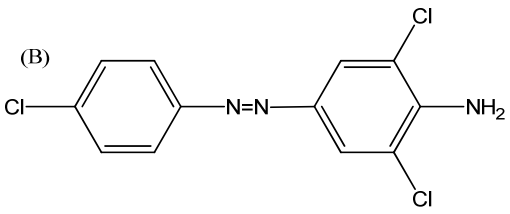
12. Choose the correct structure for the product produced in the following series of reactions.



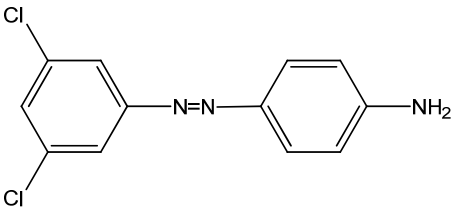

(A)



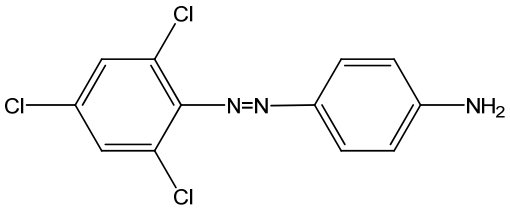

(B)



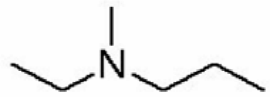

(C)




(D)

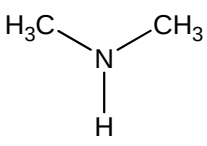


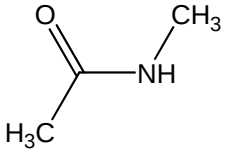
13. What is the correct name for the following amine?



A. ethyl, methyl, propylamine
B. diethyl, methylamine
C. N-ethyl-N-methylpropynamide
D. N-ethyl-N-methylpropylamine

14. Consider the chemical structures for dimethylamine and *N*-methyl-acetamide shown (the pKa values of their conjugate acids are provided). Which of the following statements regarding their chemistry is **FALSE**?



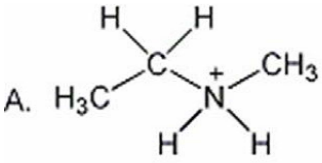


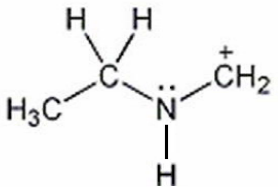
dimethylamine
pKa=10.73

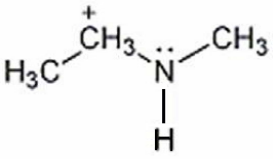
N-methyl-acetamide
pKa = 0

A. If you were presented a mixture of dimethylamine and *N*-methyl acetamide dissolved in ether, it would be possible to separate them from each other using extraction with acetic acid.
B. N-methyl acetamide is a weaker base than dimethylamine due to resonance and induction effects.
C. Upon treatment with a strong acid, the nitrogen atom of dimethylamine yields a protonated amine of pKa=10.73 and the nitrogen atom of N-methyl acetamide is protonated to give a protonated amide with pKa=0
D. Dimethyl amine will react with excess $CH_3I$ by an $S_N2$ mechanism to produce an achiral quaternary ammonium salt.

15. Which structure corresponds to the conjugate acid of $CH_3CH_2NHCH_3$?

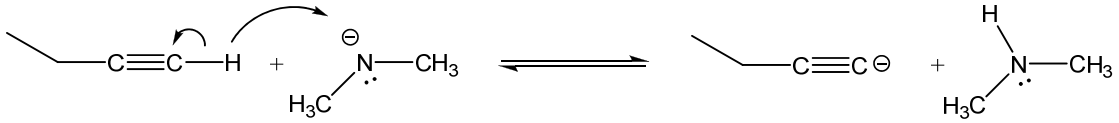
A. 

B. 

C. 

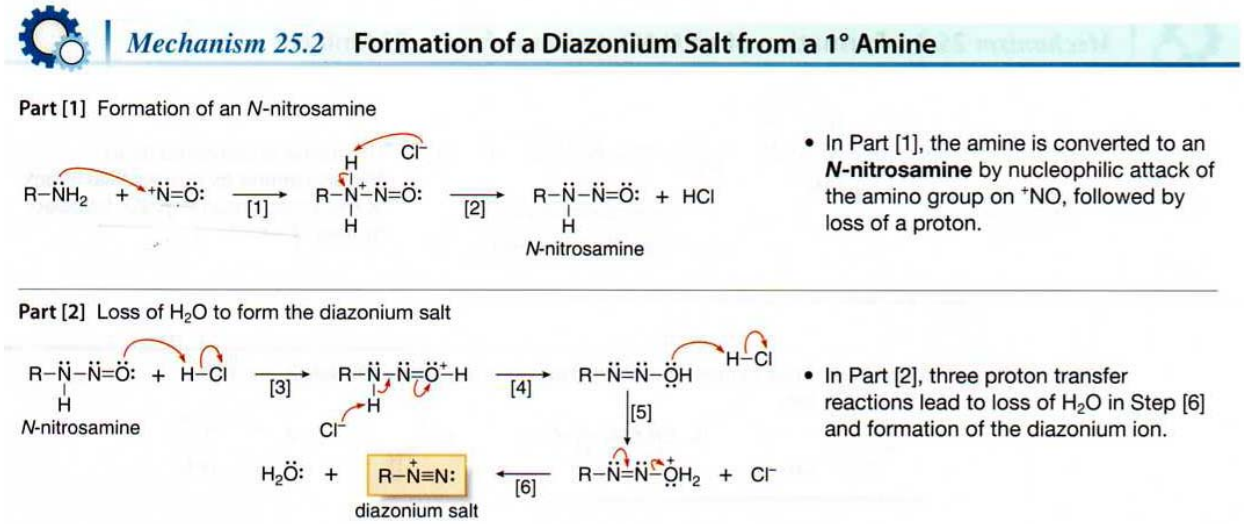
A. A
B. B
C. C

16. Which statement considering the following acid-base reaction is more **FALSE**?



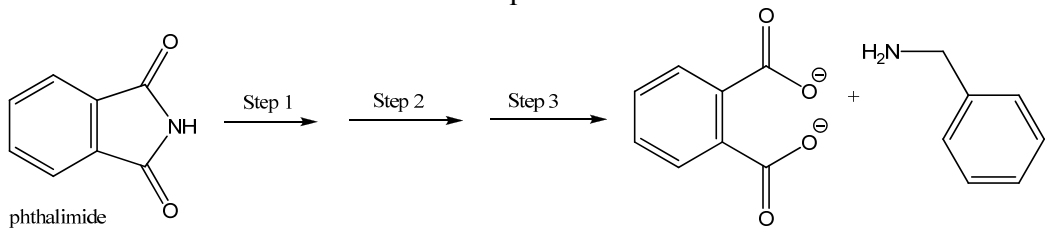
A. The pKa of 1-butyne is approximately equal to 25, that of acetylene [the anion formed from 1-butyne is slightly more basic due to the e-donating R group]
B. The pKa of dimethyl amine is approximately equal to that of methylamine, 40, considering the same approximation as in A.
C. The equilibrium of this reaction favors the products, and Keq > 1
D. To show the flow of electrons in this reaction, requires two arrows as shown

17. I have provided the mechanism from our text for formation of a diazonium salt from a 1° amine. Which statement is **TRUE** concerning the mechanism and products of this class of reactions?




A. The electrophile $^{+}NO_2$ is produced from the reaction of $NaNO_2$ and HCl
B. The reaction of a secondary amine stops at the N-nitrosamine due to the lack of an acidic hydrogen on nitrogen
C. The diazoinum ion product may react with a substituted benzene in a coupling reaction to produce an azo compound, provided that the substituted benzene possesses a strong electron-withdrawing group
D. The substitution reaction of a diazonium salt is hindered by the loss of $N_2$, a poor leaving group

18. An example Gabriel synthesis is provided. Pick the statement below that **best** describes the mechanistic details of this reaction sequence.



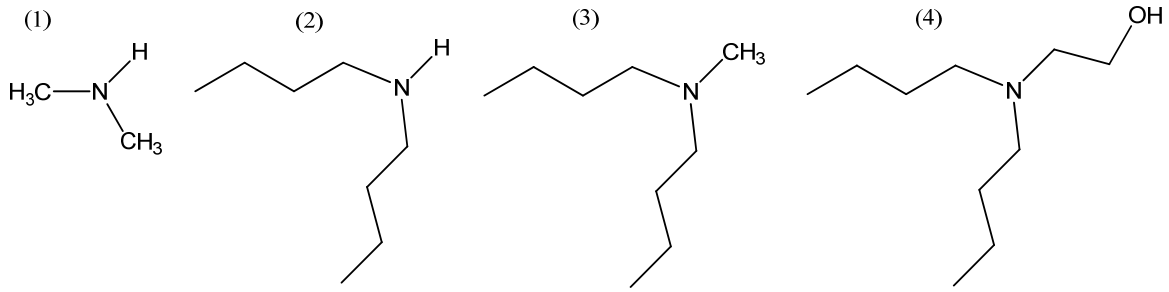

A. Phthalimide reacts with strong base to form a nitrosonium ion. This nitrosonium ion undergoes an $S_N2$ reaction to form an intermediate product that is then heated in the presence of base to form the primary amine.

B. Phthalimide undergoes a $S_N2$ reaction with a primary alkyl halide to form the primary amine directly.

C. Phthalimide is reacted with a strong base to form a highly reactive anion. This anion is then reacted with an alkyl halide, followed by reaction with Ag2O. This mixture is then heated to form the primary amine.

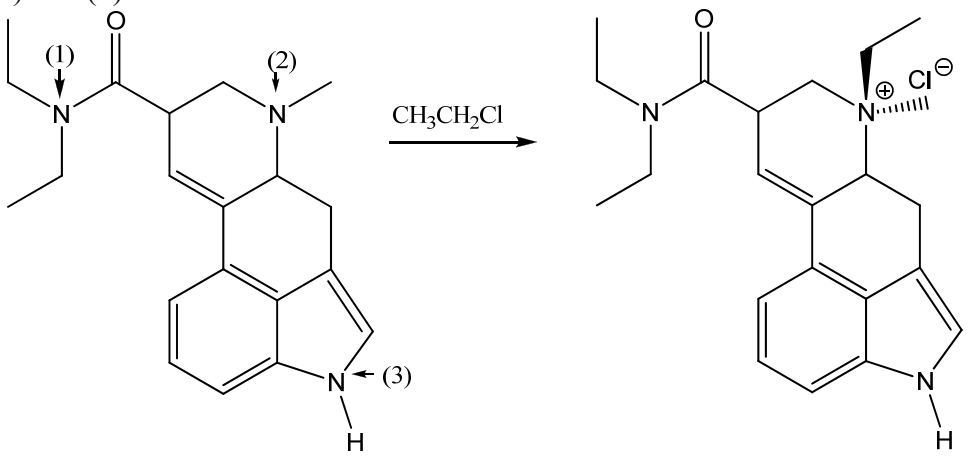
D. An acid/base reaction occurs to form the resonance stabilized anion of phthalimide and then a $S_N2$ reaction to form a substitution product. The alkylated imide is then hydrolyzed to form the primary amine.

19. Place the following compounds in order of **increasing (lowest to highest)** boiling point.




A. 1<2<3<4
B. 1<3<2<4
C. 1<4<2<3
D. 2<1<3<4

20. The following represents the N-alkylation reaction of lysergic acid diethyl amide (LSD) using ethyl chloride. LSD has three nitrogen containing functional groups denoted with (1), (2) and (3). Which one of the statements is **FALSE**?




A. The amide nitrogen (1) is a weak base due to resonance stabilization and the induction effect of C=O
B. The 2° amine (3) is a weak base due to resonance stabilization of the lone pair into the extended π system of the neighboring aromatic ring
C. 3° amine nitrogen (2) is the strongest base and most nucleophilic of the 3 nitrogen atoms of LSD
D. The alkylation reaction shown converts the nitrogen atom (2) into a quaternary ammonium compound, but we need not consider stereochemistry due to the interconversion of the two enantiomers