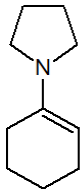
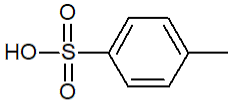
20.12: SOLUTIONS TO ADDITIONAL EXERCISES

20-1 Amine A is the more basic of the two amines. Since its lone pair of electrons cannot resonance into the ring like that of amine B, it is more basic. Amine B can delocalize its electrons, making it a weaker base but a stronger acid.

20-2

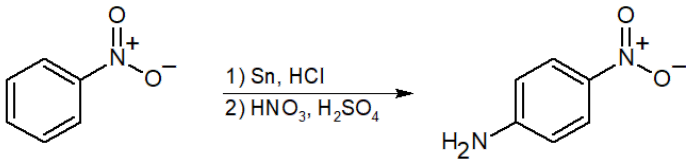


20-3



4-methylbenzene-1-sulfonic acid

20-4



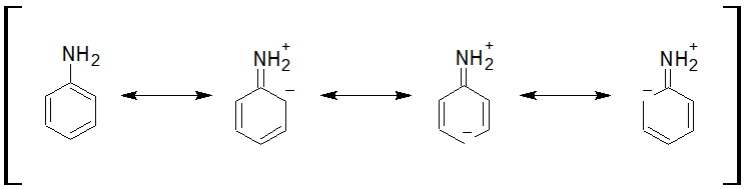
20-5 Answer: C

20-6 This reaction is not the best way to synthesize ethanamine because of the high ratio of mixed products obtained. Because the reaction occurs so fast, we are unable to stop the reaction at only the primary alkylation; the amine will continue on to make many secondary and tertiary amines in addition to our desired product.

Basicity and Effects of Amines

20-7:

Cyclohexanamine has no resonance structure that can contribute to delocalizing its lone pair of electrons.



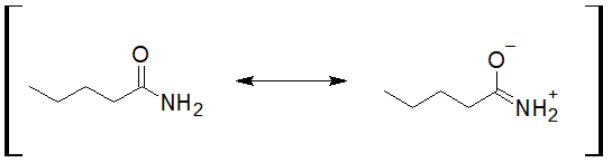
20-8:

Unlike on the para- and ortho-nitroaniline isomers, m-nitroaniline's nitro and amine groups cannot form any resonance structures to delocalize their pi-electrons with each other, making m-nitroaniline the most basic.

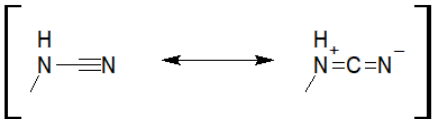
20-9:

a) and d) have no pi-acceptors directly attached to the amine.

b)



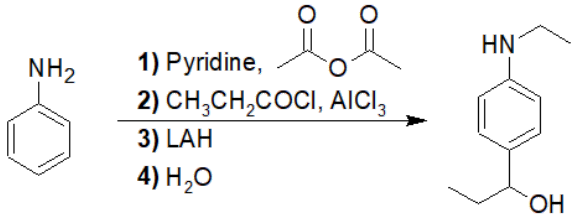
c)



Aromatic Substitution of Arylamines and Pyridine

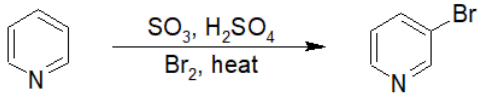
20-10:

If a protecting group is not placed on the amino group of aniline, it will form a complex with AlCl3 during the acylation step of the reaction and prevent the reaction from occurring. By placing a protecting group on the amine, we still maintain an activated ring that can give us ortho- or para- substituted products, but won't interfere with the reaction itself.

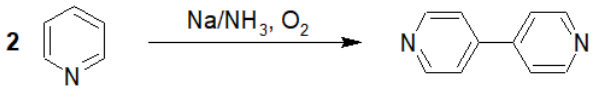


20-11:

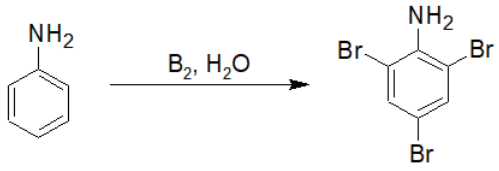
a)



b)



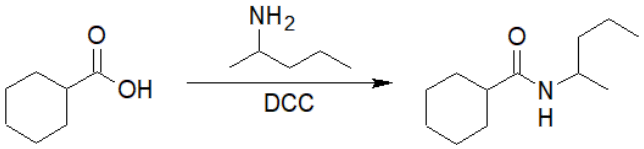
20-12:



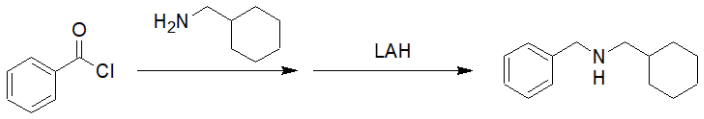
2,4,6-tribromoaniline

Alkylation and Acylation of Amines

20-13:

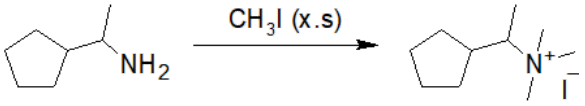


20-14:



20-15:

Answer: A

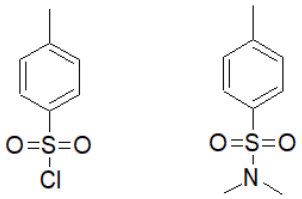


Formation of Sulfonamides

20-16:

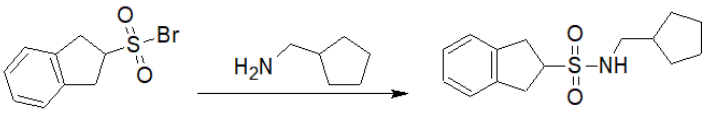
Answer: C

20-17:



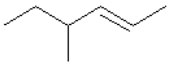
A **B**

20-18:



Amines as Leaving Groups: The Hofmann Elimination

20-19:



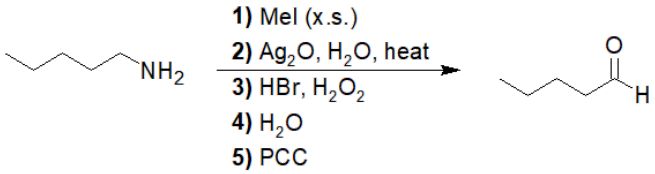
(2*E*)-4-methylhex-2-ene

20-20:

Answer: D

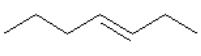
20-21:

Possible route of synthesis:



Oxidation of Amines: The Cope Elimination

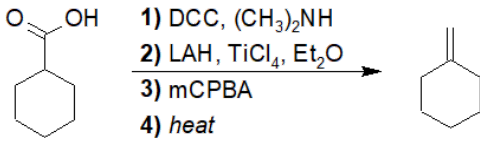
20-22:



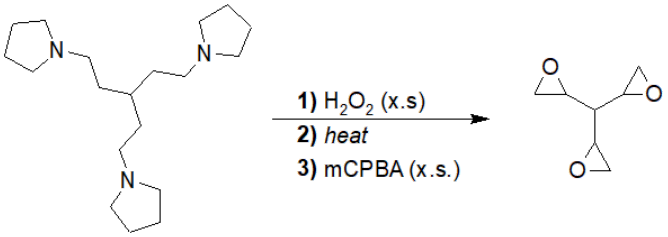
(3*E*/*Z*)-hept-3-ene

20-23:

Possible route of synthesis:

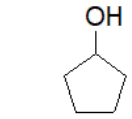


20-24:



Reactions of Amines with Nitrous Acid

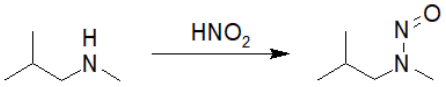
20-25:



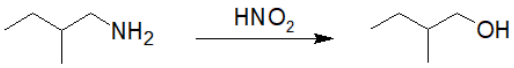
cyclopentanol

20-26:

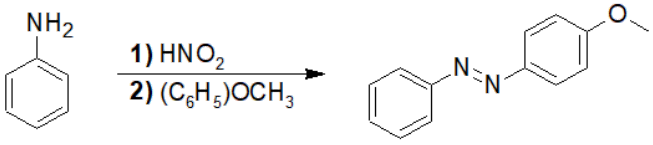
a)



b)

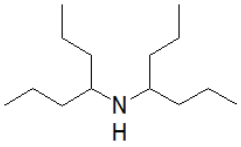


20-27:



Synthesis of Amines by Reductive Amination and Acylation-Reduction

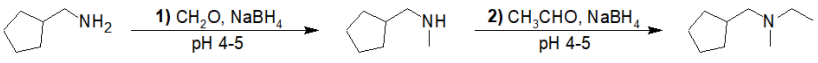
20-28:



***N*-(heptan-4-yl)heptan-4-amine**

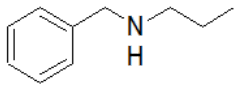
20-29:

Answer: B



20-30:

Answer: C



***N*-benzylpropan-1-amine**
