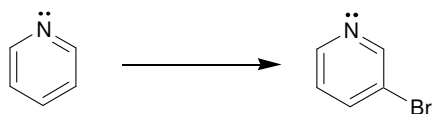
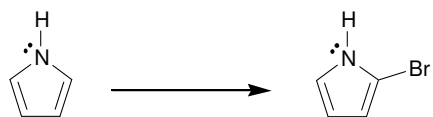
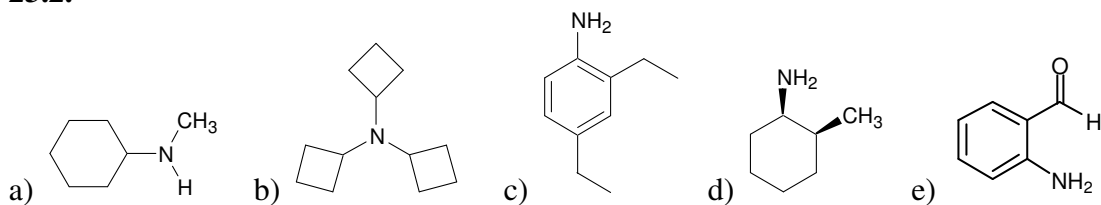
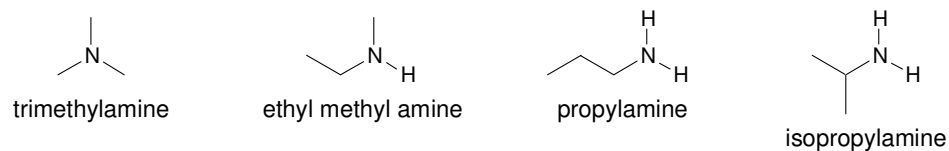
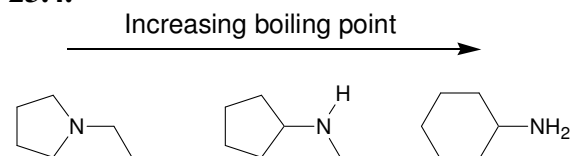


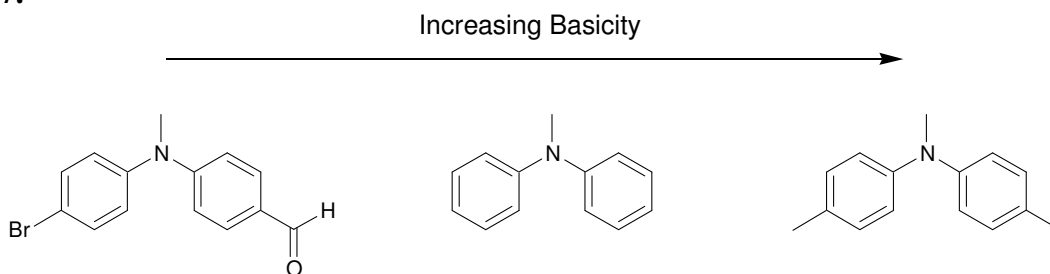
**Reactions of Nitrogen Heterocycles****Solutions****23.1.**

- a) 3,3-dimethyl-1-butanamine
- b) cyclopentylamine
- c) *N,N*-dimethylcyclopentylamine
- d) triethylamine
- e) (*1S,3R*)-3-isopropylcyclohexanamine
- f) (*1S,3S*)-3-aminocyclohexanol

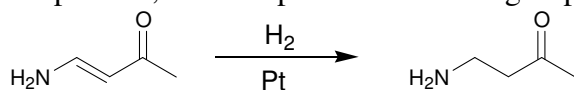
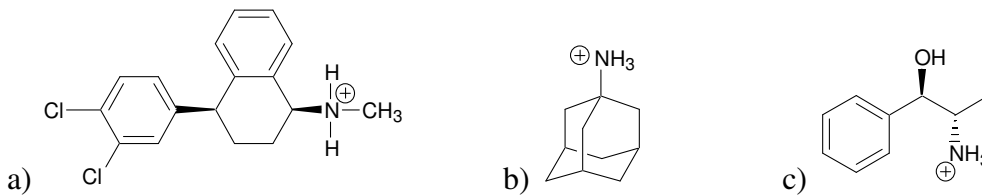
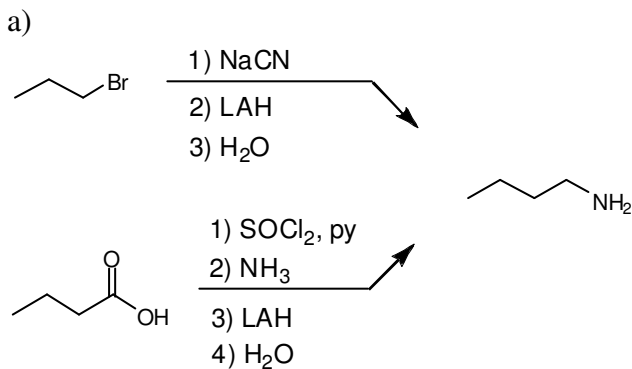
**23.2.****23.3.****23.4.**

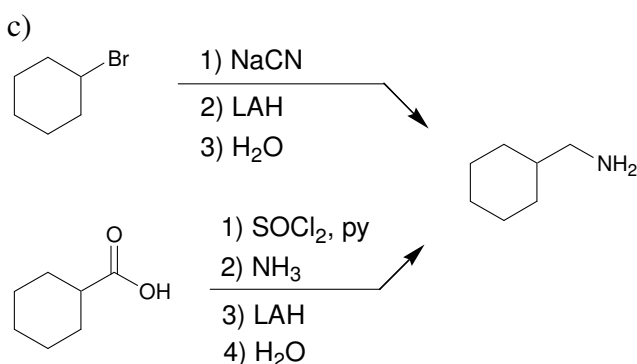
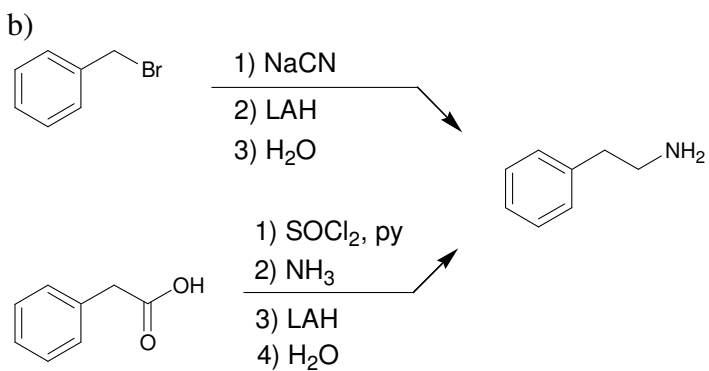
**23.5.**

- a) No. This compound has eight carbon atoms and only one functional group.  
 b) Yes.  
 c) Yes.

**23.6.****23.7.**

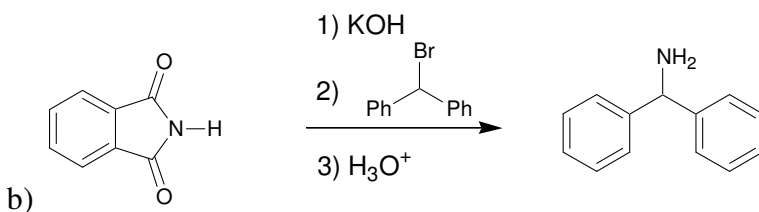
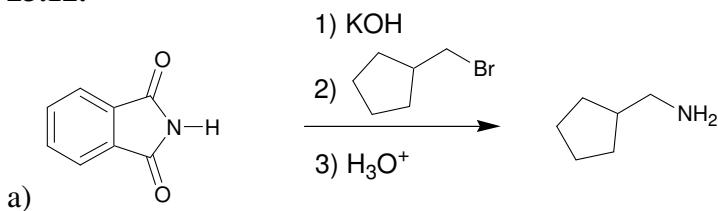
**23.8.** In the reactant, the lone pair of the amino group is delocalized via resonance. In the product, the lone pair of the amino group is localized.

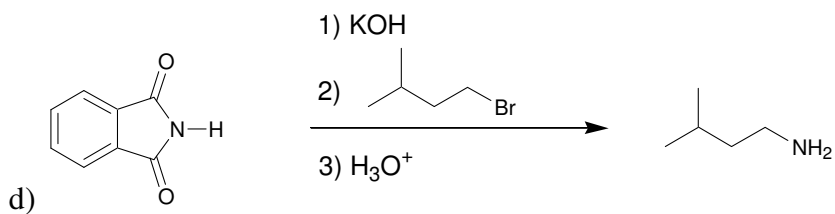
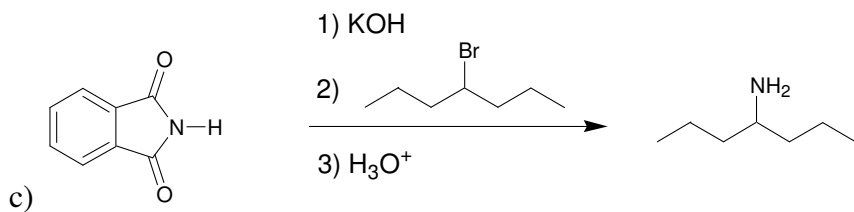
**23.9.****23.10.**



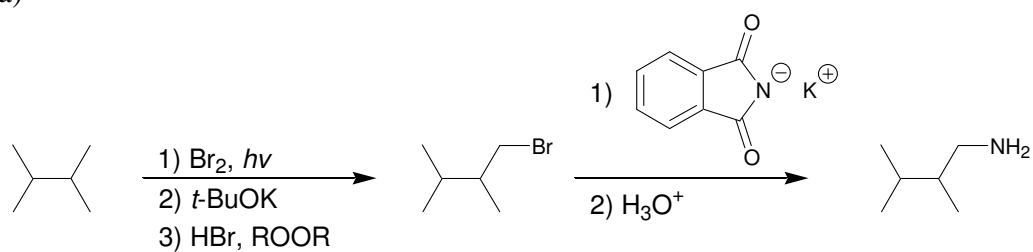
**23.11.** This compound cannot be prepared from an alkyl halide or a carboxylic acid, using the methods described in this section, because there are two methyl groups at the alpha position (the carbon atom connected to the amino group). These two methyl groups cannot be installed with either of the synthetic methods above, because both methods produce an amine with two alpha protons.

**23.12.**

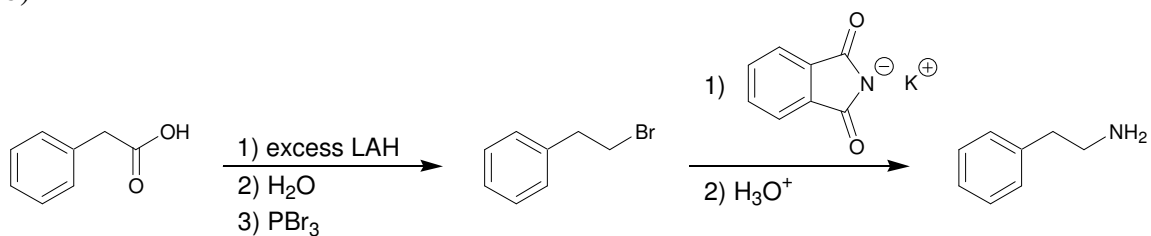



**23.13.**

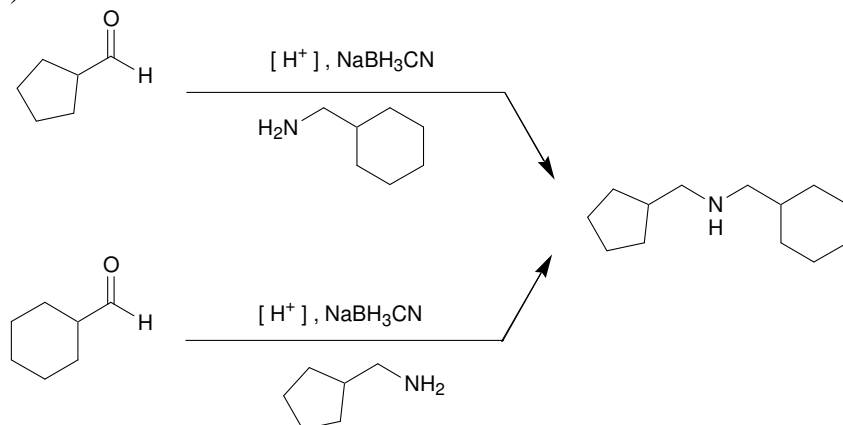
a)



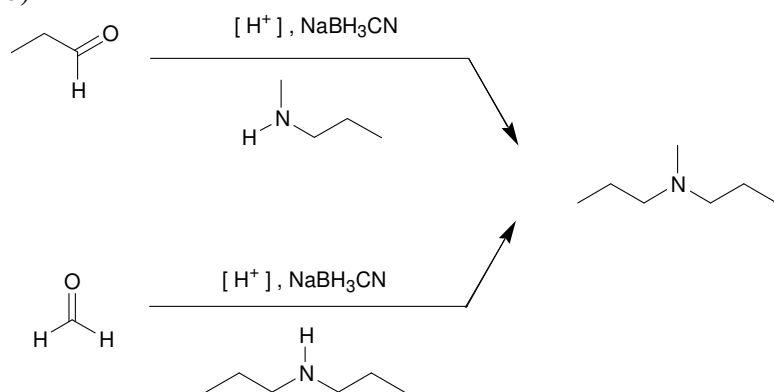
b)


**23.14.**

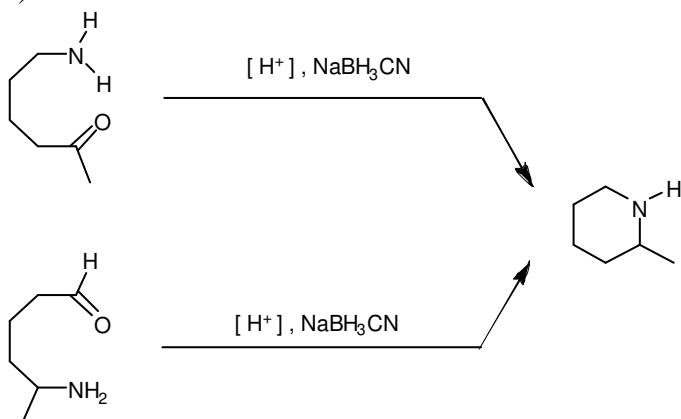
a)



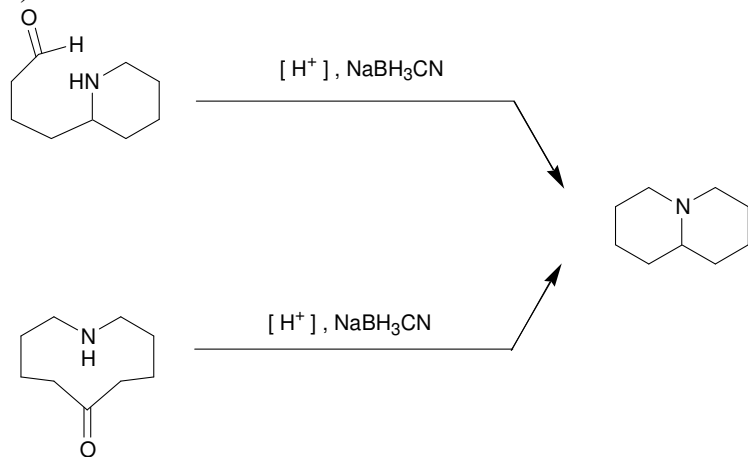
b)

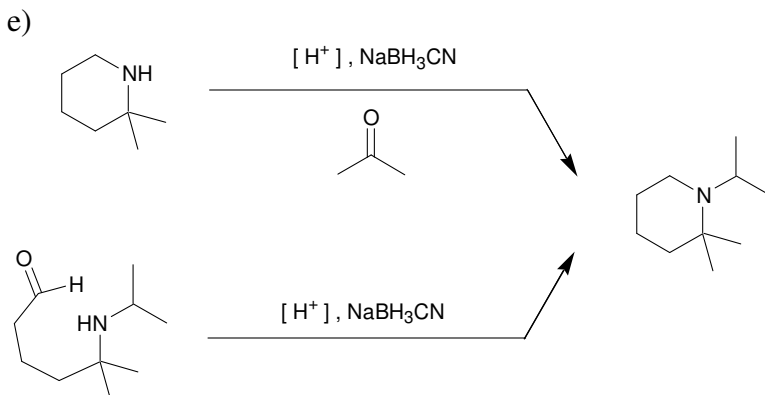
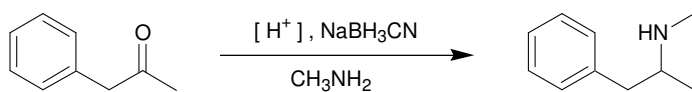


c)

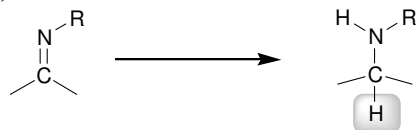


d)

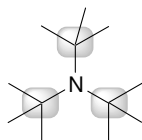


**23.15.**

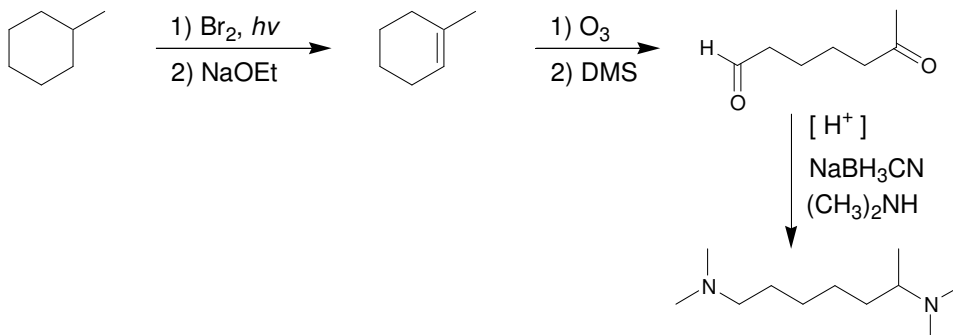
**23.16.** The last step of reductive amination is the reduction of a  $C=N$  bond. That step introduces a proton on the alpha position (the carbon atom that is connected to the nitrogen atom in the product):



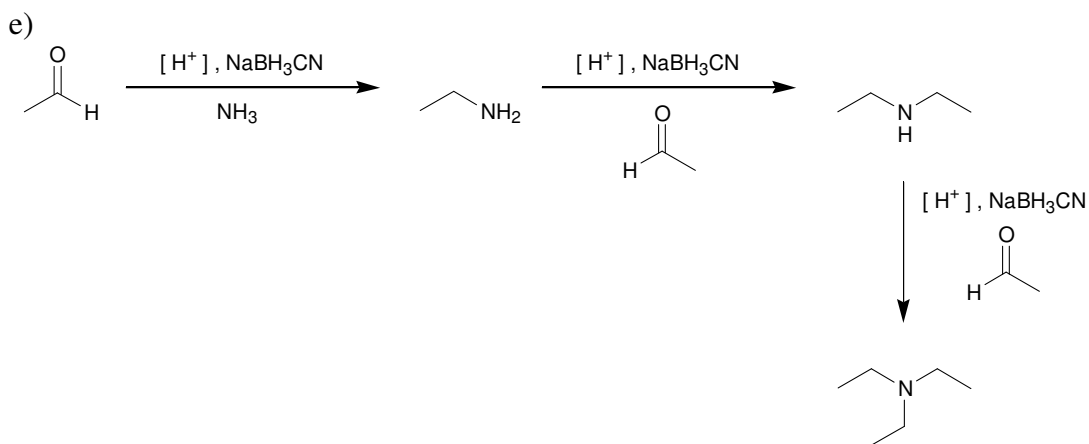
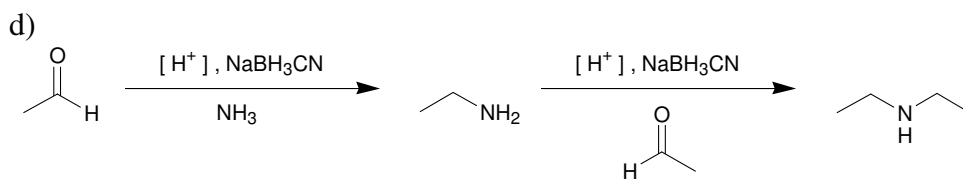
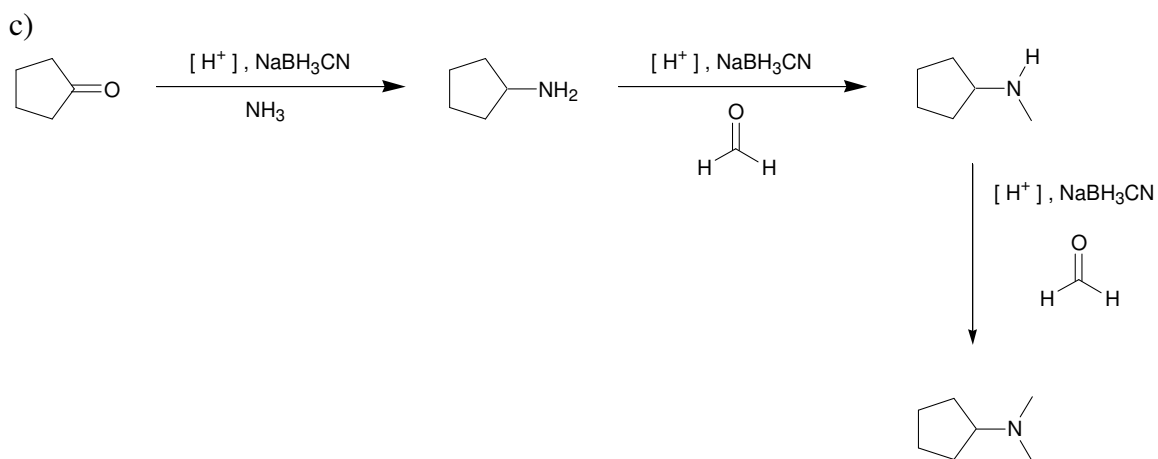
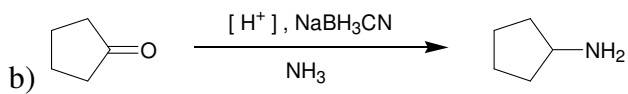
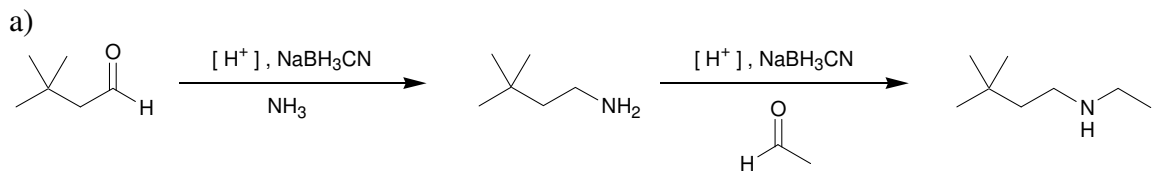
As a result, the product of a reductive amination must have at least one proton at the alpha position. In the case of tri-*tert*-butyl amine, there are three alpha positions, and none of them bears a proton. Each of the alpha positions has three alkyl groups and no protons.

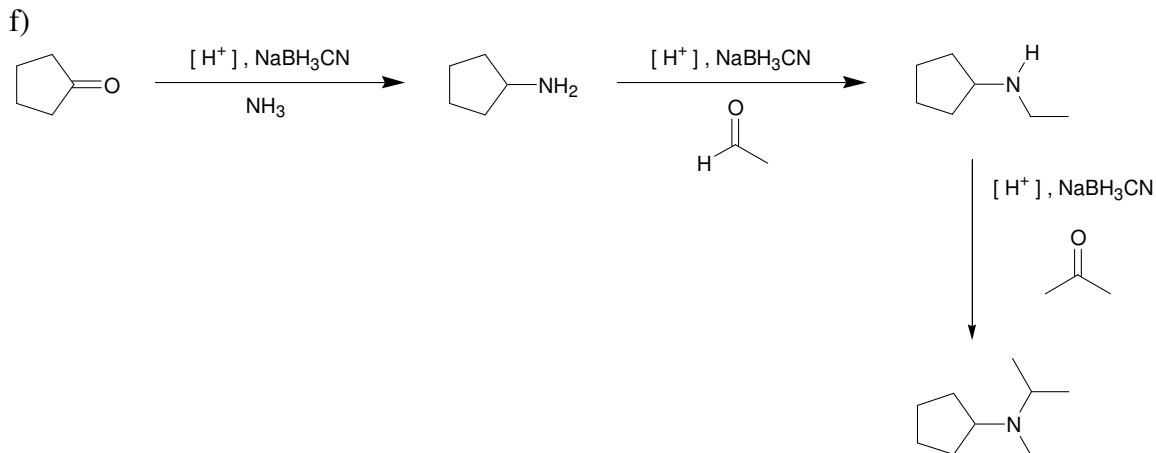


Therefore, this compound cannot be made with a reductive amination.

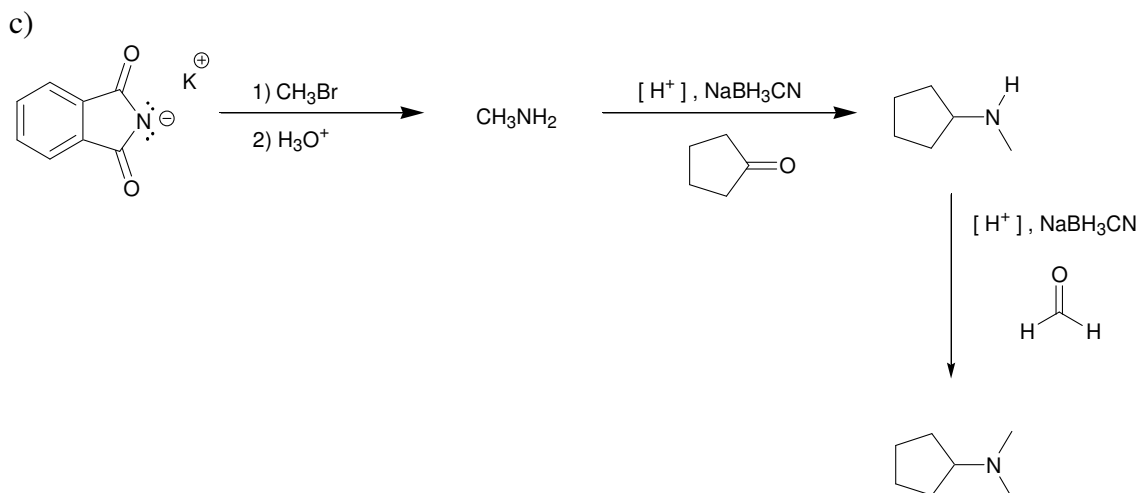
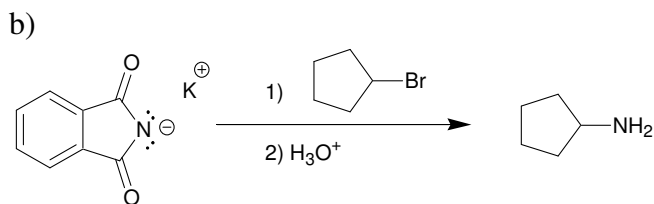
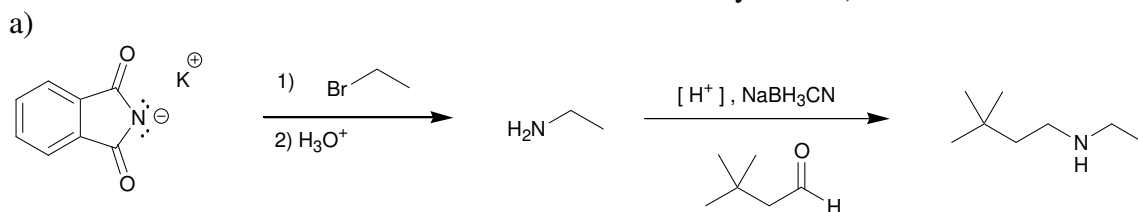
**23.17.**

## 23.18.



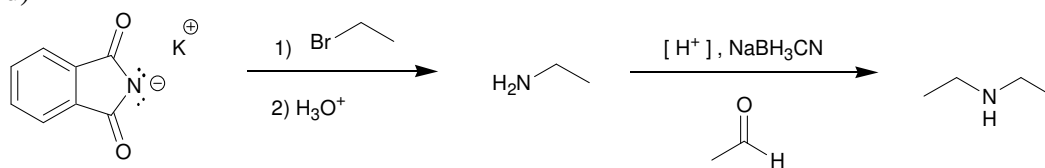


**23.19.** The first alkyl group is installed via a Gabriel synthesis, and the remaining alkyl groups are installed via reductive amination processes. For most of the following syntheses, there is a choice regarding which group to attach via the initial Gabriel synthesis. In such cases, the least sterically hindered group is chosen (the group whose installation involves the least hindered alkyl halide):

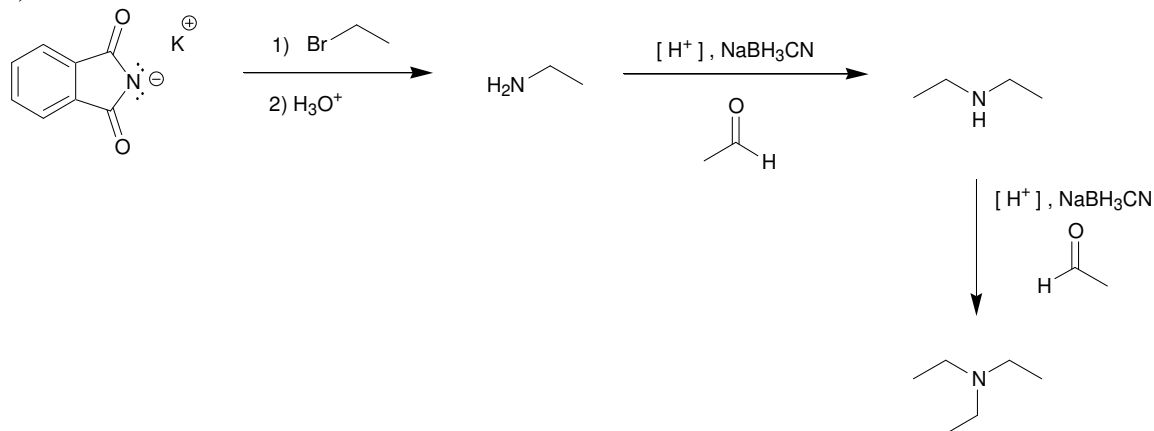




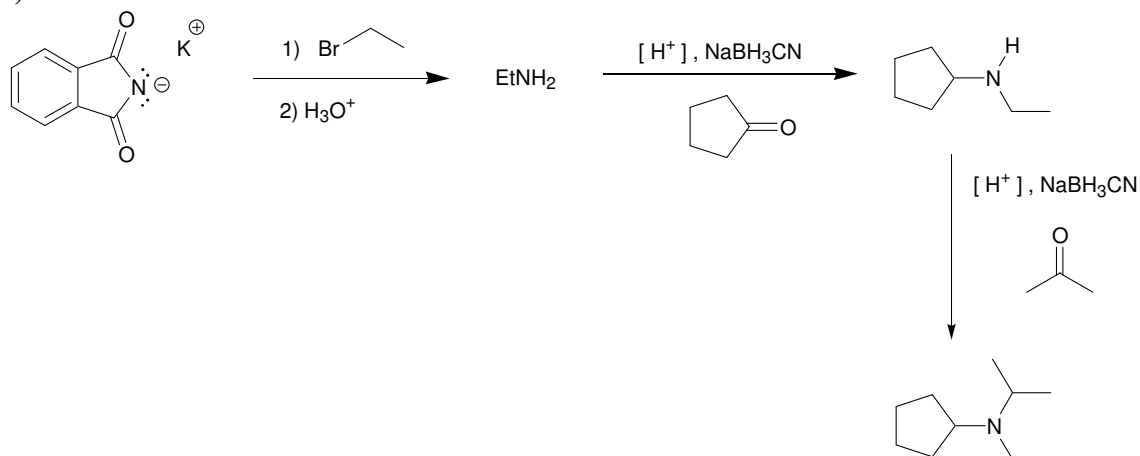
d)



e)

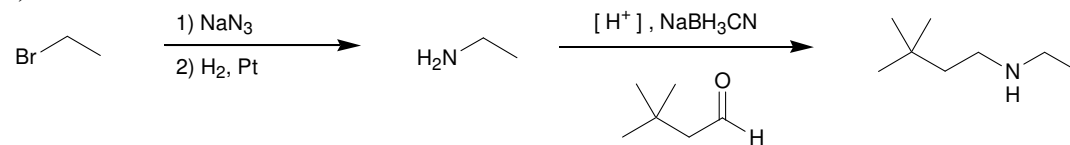


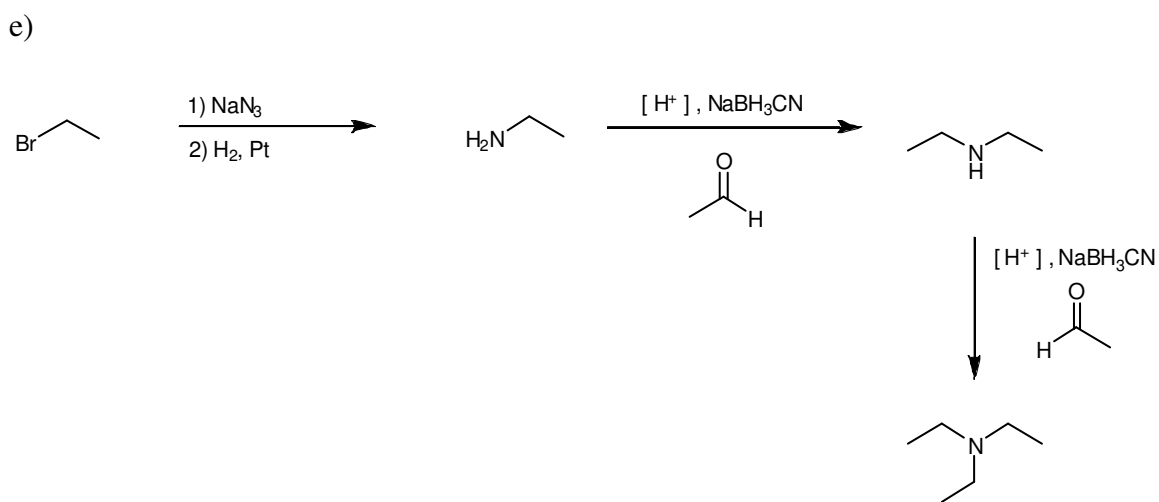
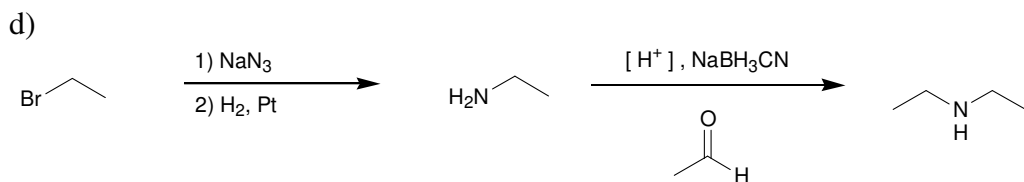
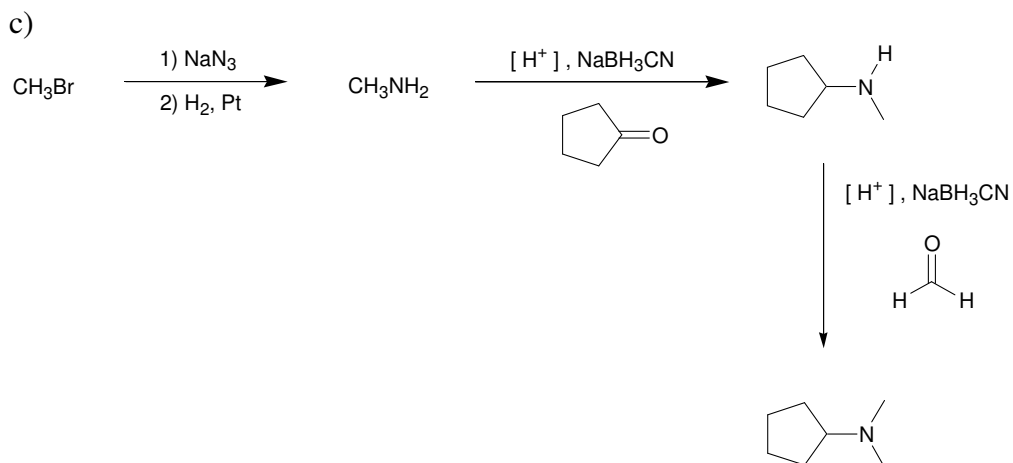
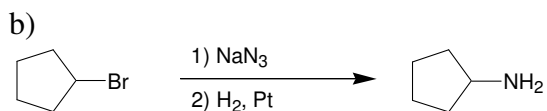
f)



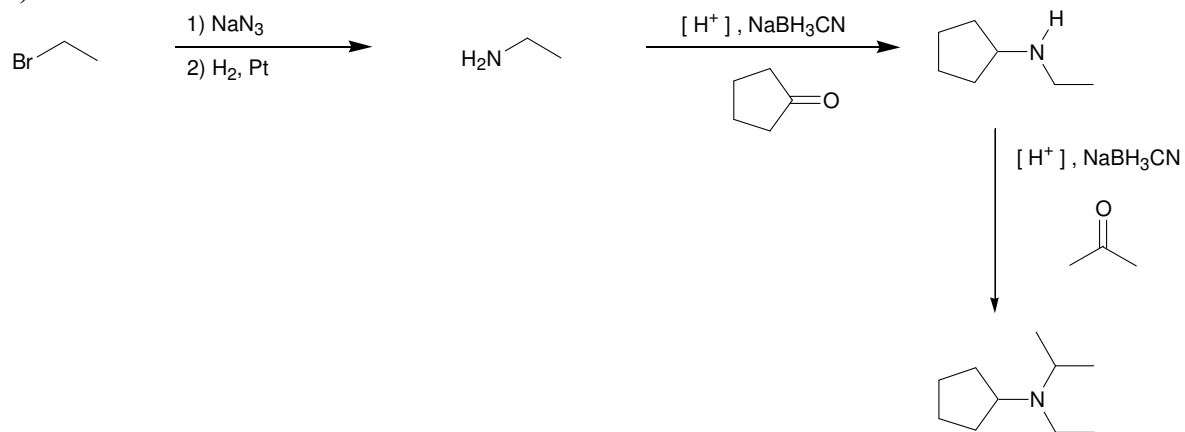
**23.20.** The first alkyl group is installed via an azide synthesis, and the remaining alkyl groups are installed via reductive amination processes. For most of the following syntheses, there is a choice regarding which group to attach via the initial azide synthesis. In such cases, the least sterically hindered group is chosen (the group whose installation involves the least hindered alkyl halide):

a)

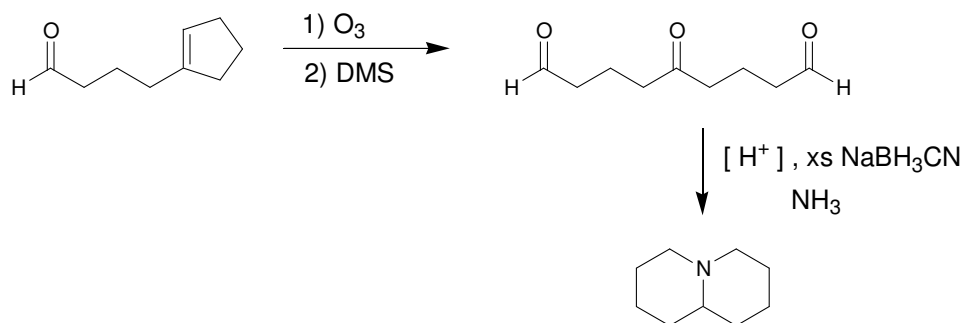




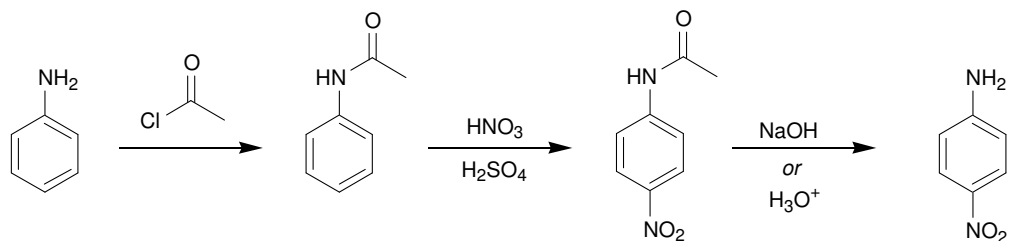
f)



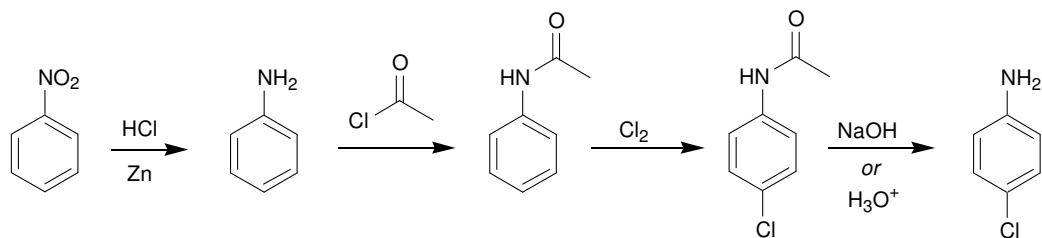
23.21.



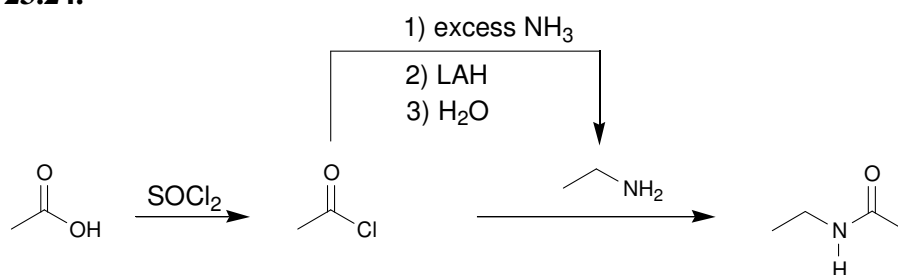
23.22.



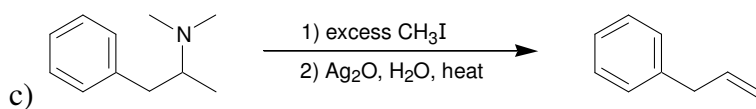
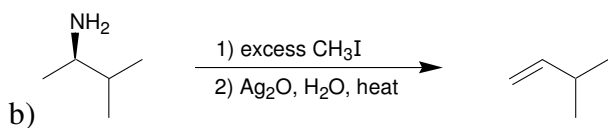
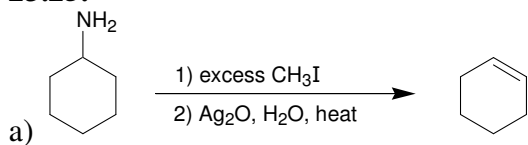
23.23.



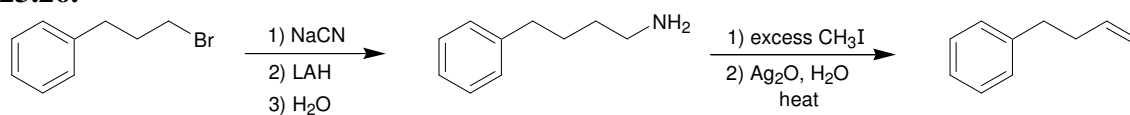
23.24.



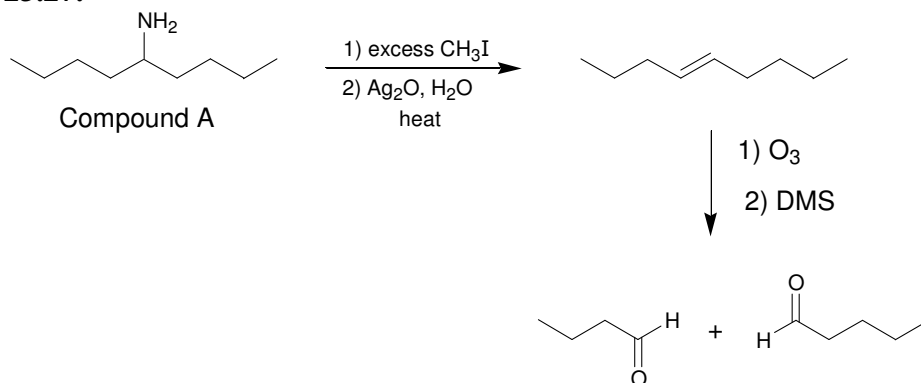
23.25.



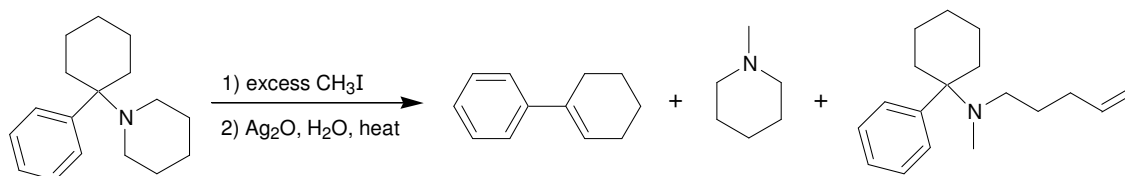
23.26.



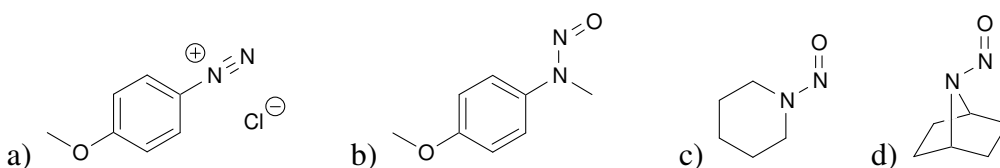
23.27.



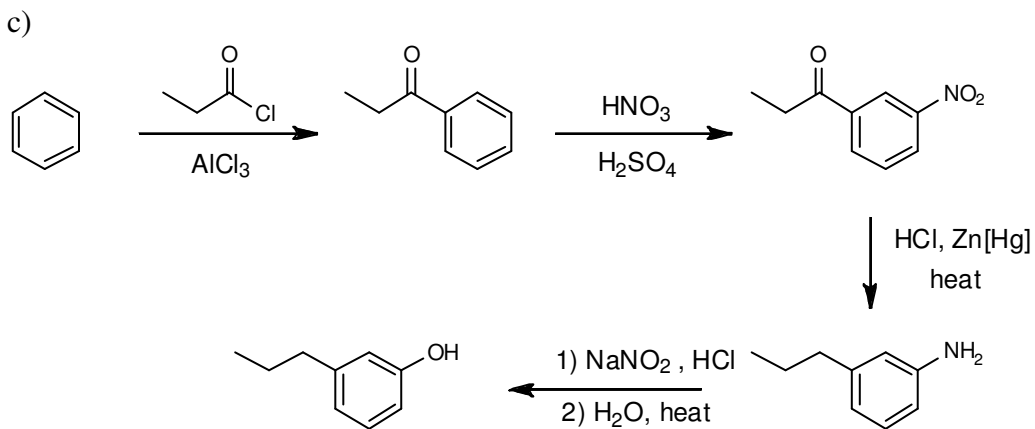
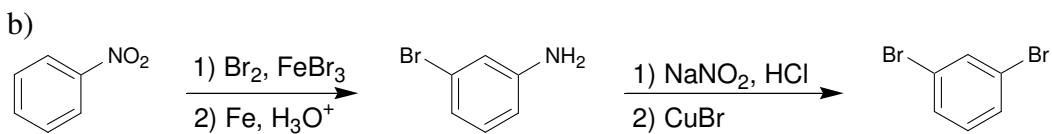
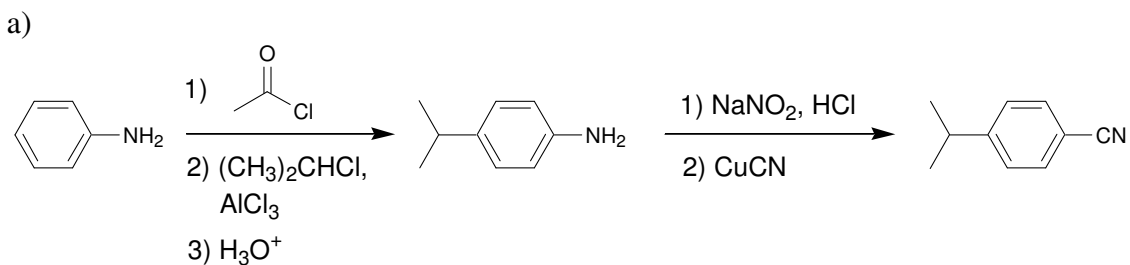
## 23.28.



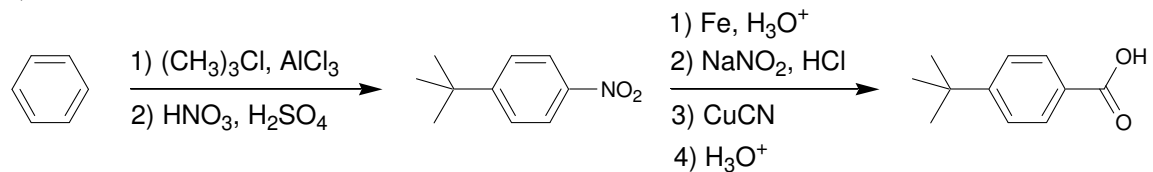
## 23.29.



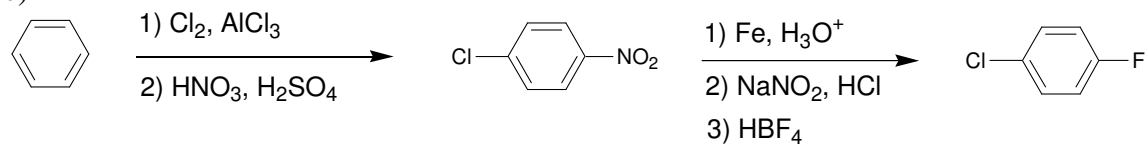
## 23.30.



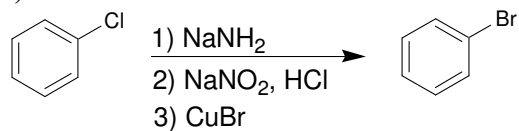
d)



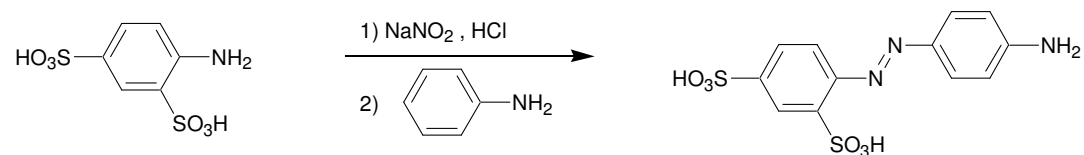
e)



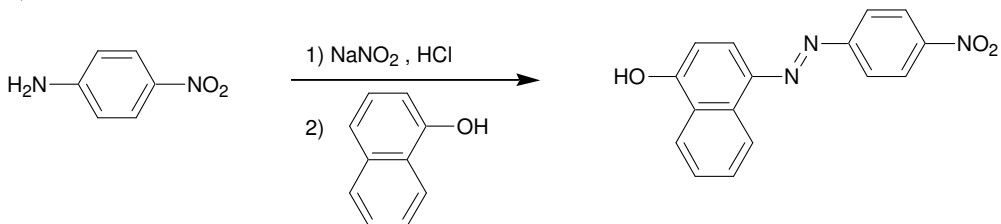
f)

**23.31.**

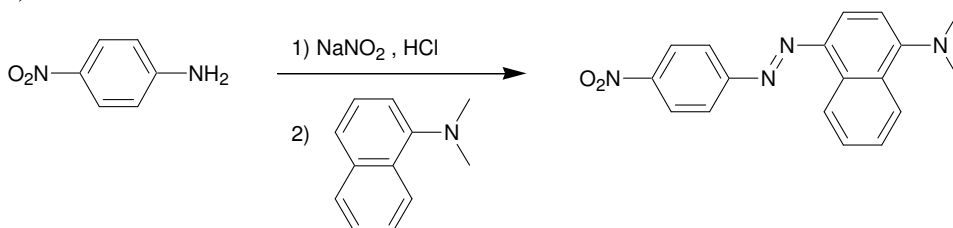
a)



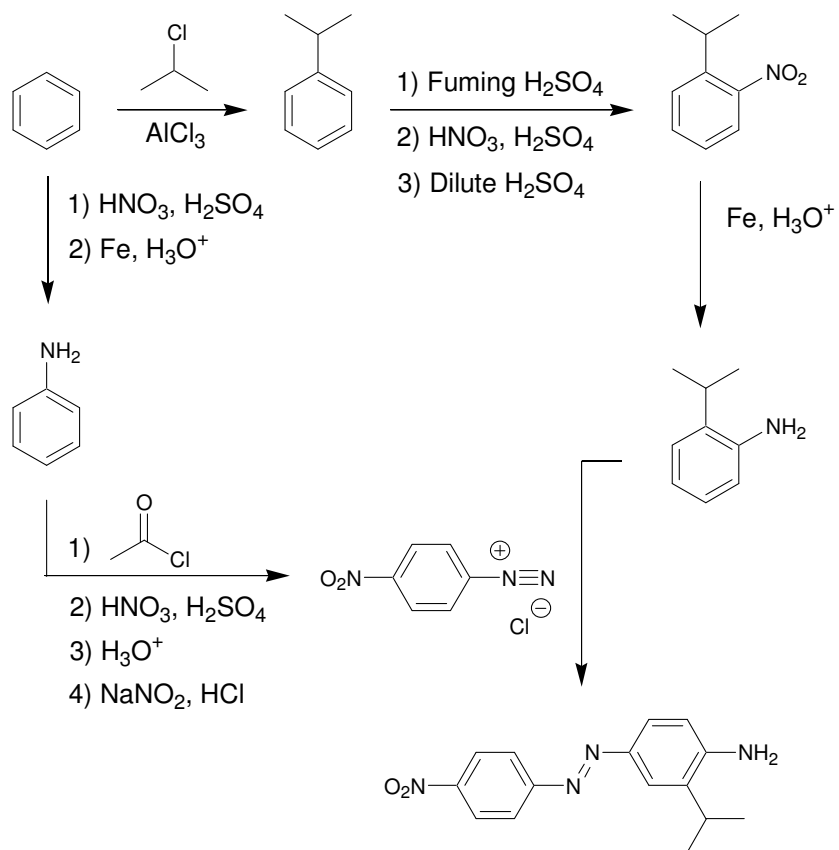
b)



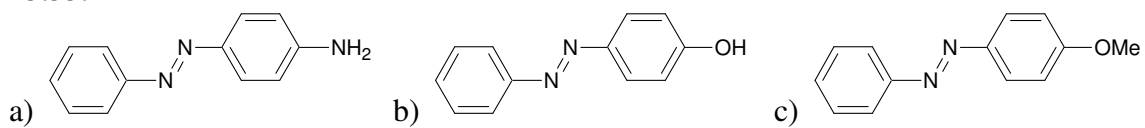
c)



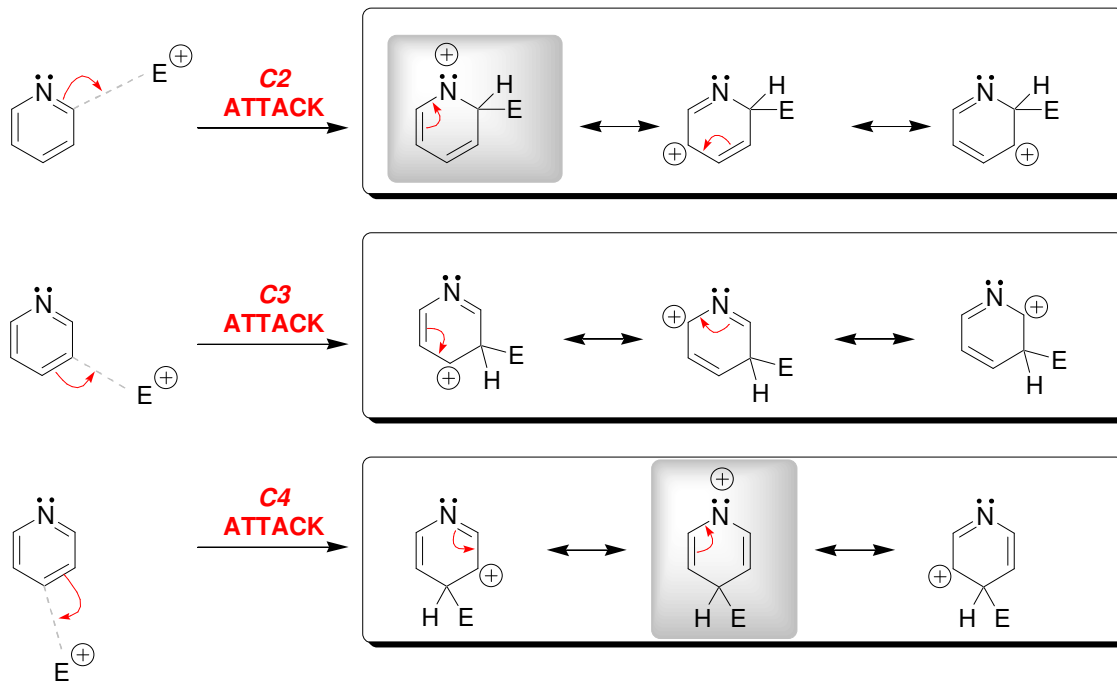
## 23.32.



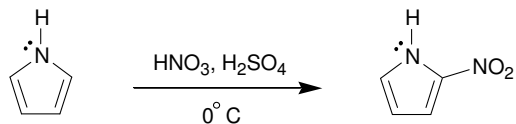
## 23.33.



**23.34.** Attack at either C2 or C4 generates an intermediate that exhibits a resonance structure with a nitrogen atom that lacks an octet (highlighted below). Attack at C3 generates a more stable intermediate:



**23.35.**



**23.36.**

a) The second compound will have an N-H stretching signal between  $3300$  and  $3500\text{ cm}^{-1}$ . The first compound will not have such a signal.

b) When treated with HCl, the first compound will be protonated to form an ammonium salt that will produce an IR signal between  $2200$  and  $3000\text{ cm}^{-1}$ . The second compound is not an amine and will not exhibit the same behavior.

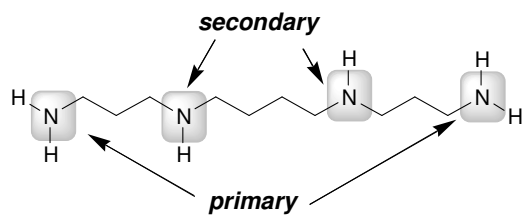
**23.37.**

a) The  $^1H$  NMR spectrum of the first compound will have a singlet resulting from the N-methyl group.  $^1H$  NMR spectrum of the second compound will not have any singlets.

b) The  $^1H$  NMR spectrum of the first compound will have six signals, while the  $^1H$  NMR spectrum of the second compound will have only three signals.



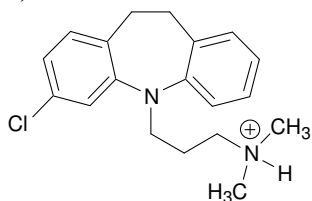
## 23.38.



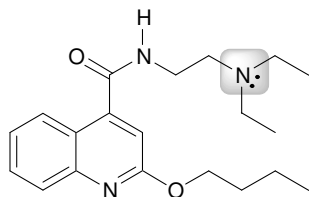
## 23.39.

a) The lone pair that is farthest away from the rings is the most basic, because its lone pair is localized. The lone pair of the other nitrogen atom is delocalized via resonance.

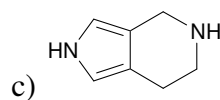
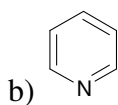
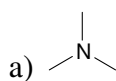
b)



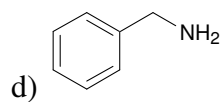
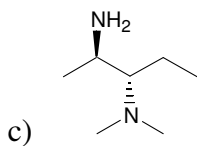
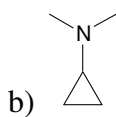
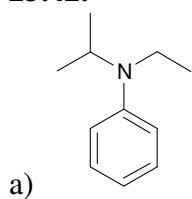
## 23.40.



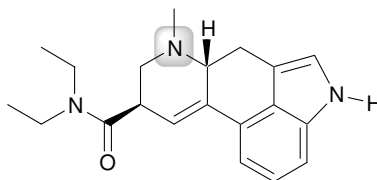
## 23.41.



## 23.42.



**23.43.** Only one of the nitrogen atoms has a localized lone pair (highlighted in the following structure). The other two nitrogen atoms have delocalized lone pairs.



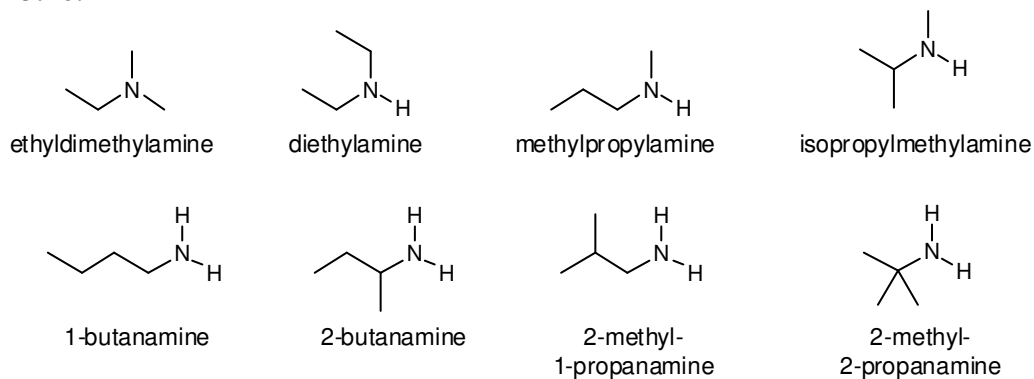
**23.44.**

a) two            b) two            c) one

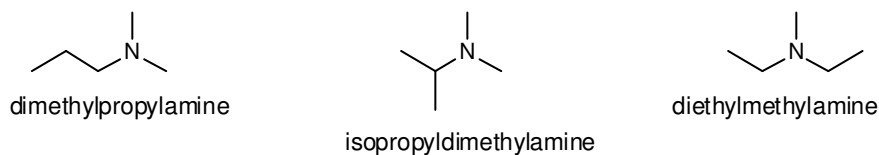
**23.45.**

- a) 2,2,3,3-tetramethyl-1-hexanamine
- b) (*S*)-4-amino-2,2-dimethylcyclohexanone
- c) dicyclobutylmethanamine
- d) 3-bromo-2,6-dimethylaniline
- e) *N,N*-dimethyl-3-propylaniline
- f) 2,5-diethyl-*N*-methyl pyrrole

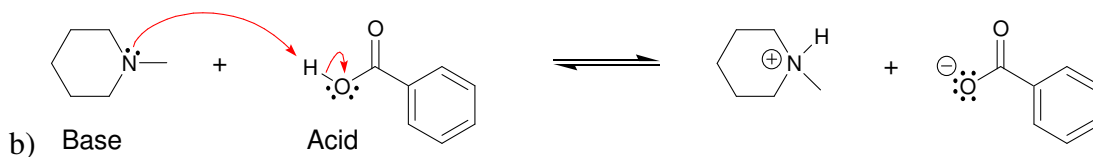
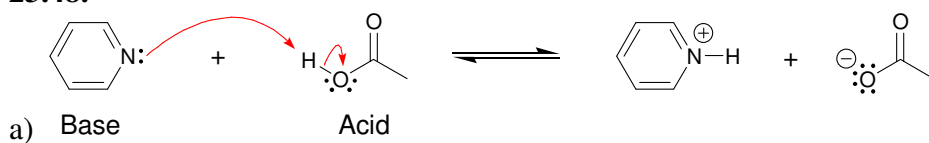
**23.46.**



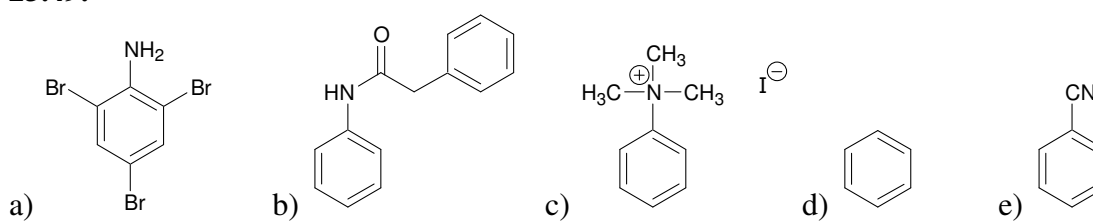
**23.47.** None of these compounds are chiral.



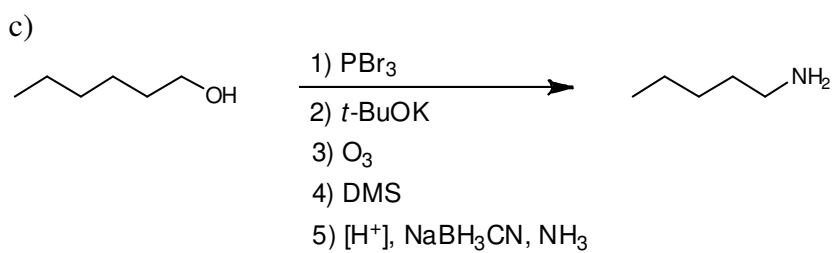
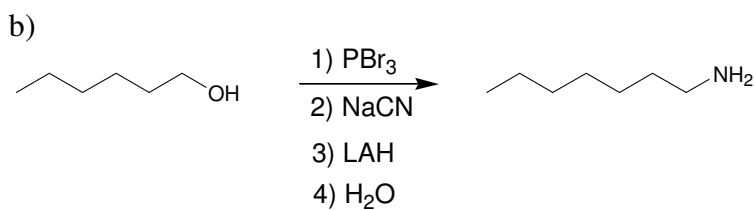
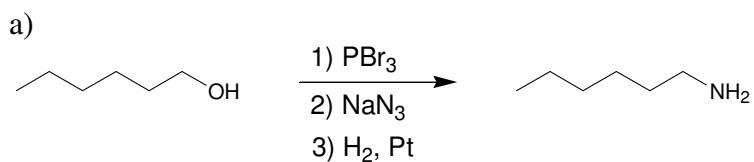
## 23.48.

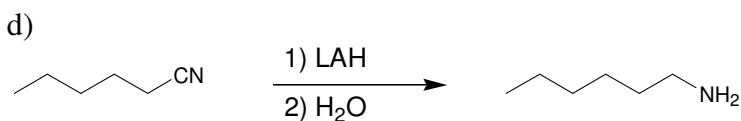
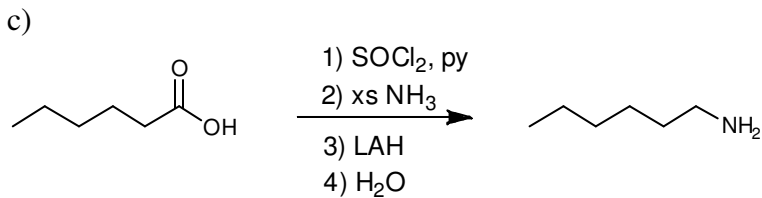
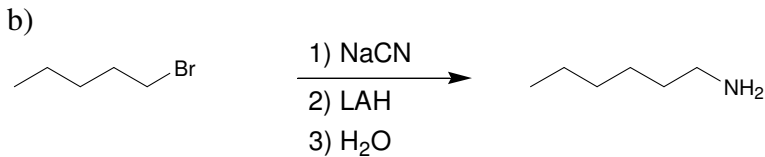
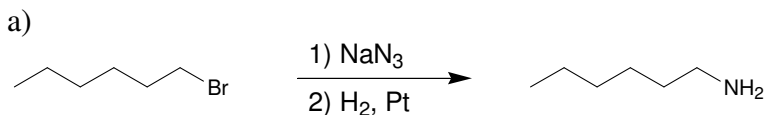


## 23.49.

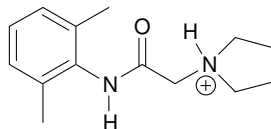
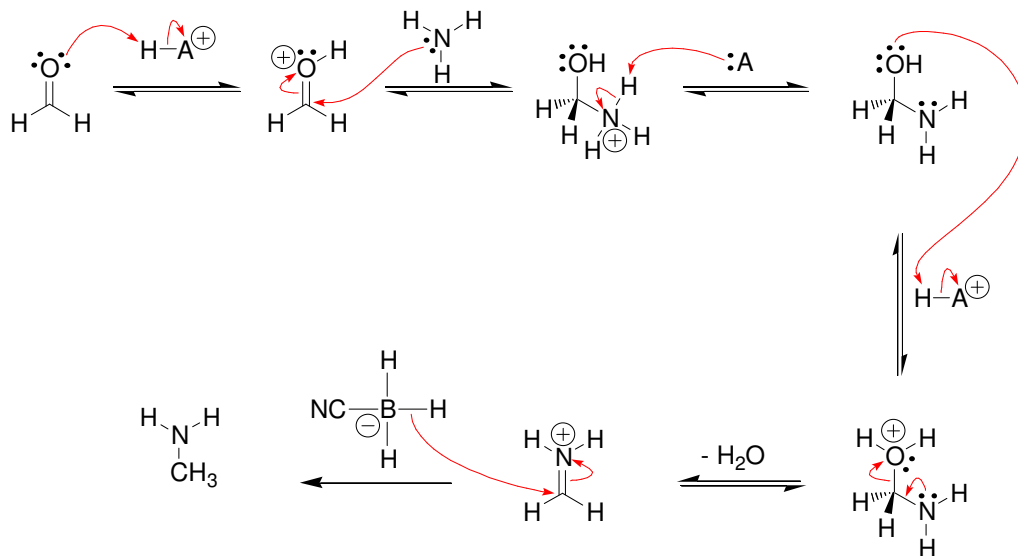


## 23.50.



**23.51.**


**23.52.** Aziridine has significant ring strain, which would increase significantly during pyramidal inversion. This provides a significant energy barrier that prevents pyramidal inversion at room temperature.

**23.53.**

**23.54.**


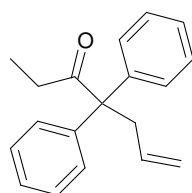
**23.55.** In acidic conditions, the amino group is protonated to give an ammonium ion. The ammonium group is a powerful deactivator and meta-director.

**23.56.**

a) The presence of the nitro group in the para position helps stabilize the conjugate base via resonance. As seen in chapter 19, this effect only occurs when the nitro group is in the ortho and para positions.

b) The basicity of *ortho*-nitroaniline should be closer in value to *para*-nitroaniline.

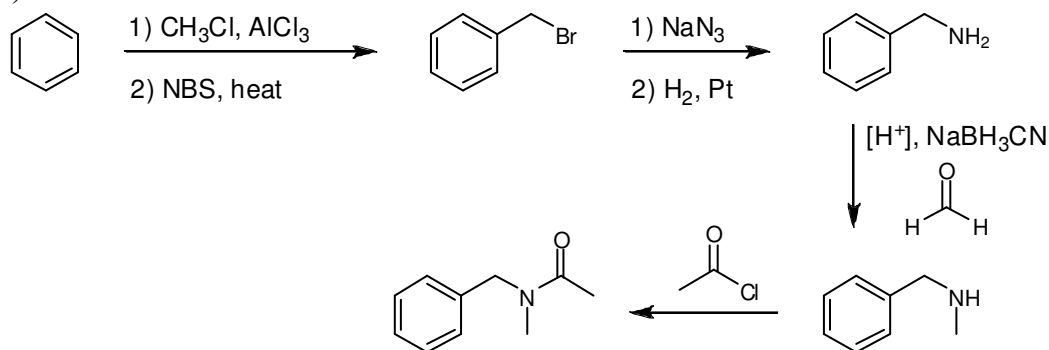
**23.57.**



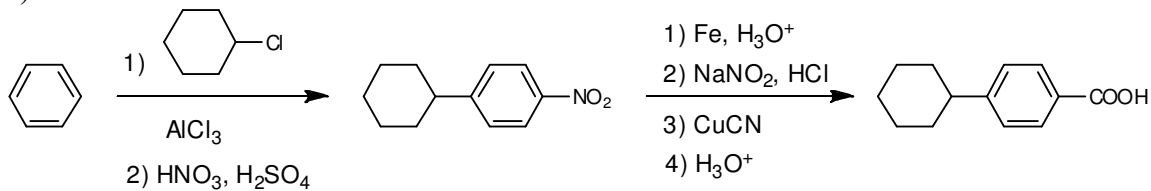
**23.58.** Protonation of the oxygen atom gives a resonance stabilized cation (as seen in chapter 20). In contrast, protonation of the nitrogen atom gives a cation that is not resonance stabilized.

**23.59.**

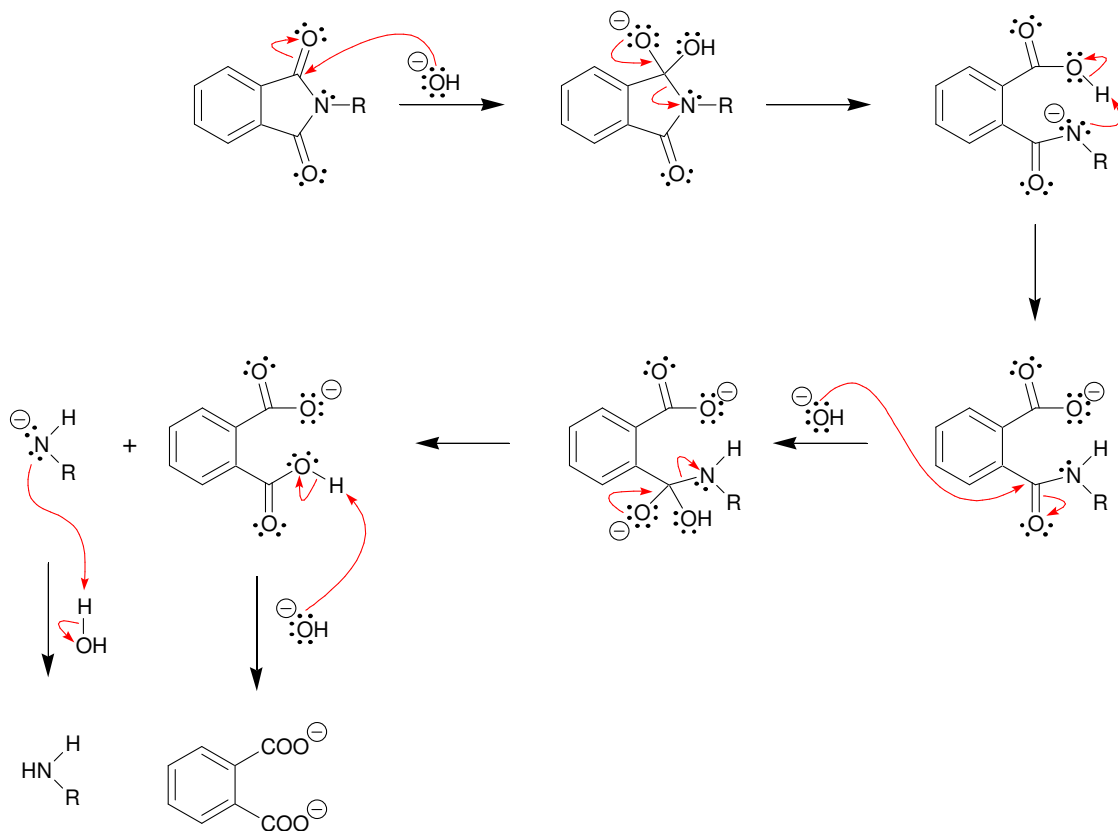
a)



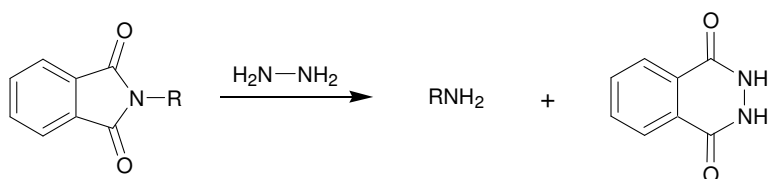
b)



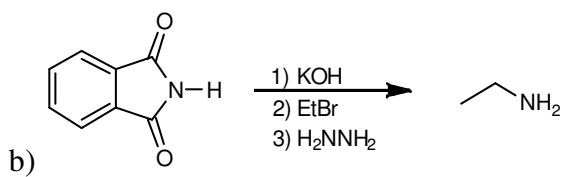
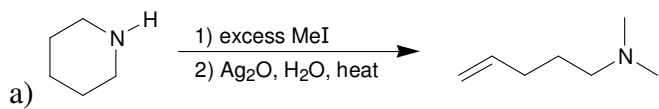
23.60.

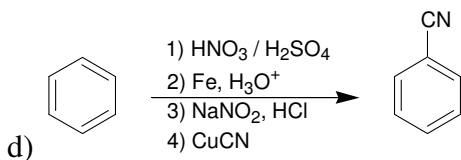
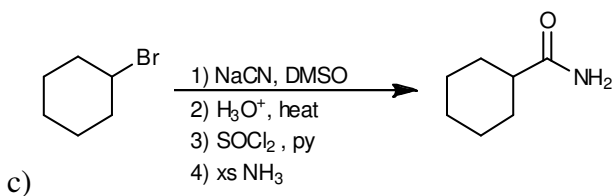
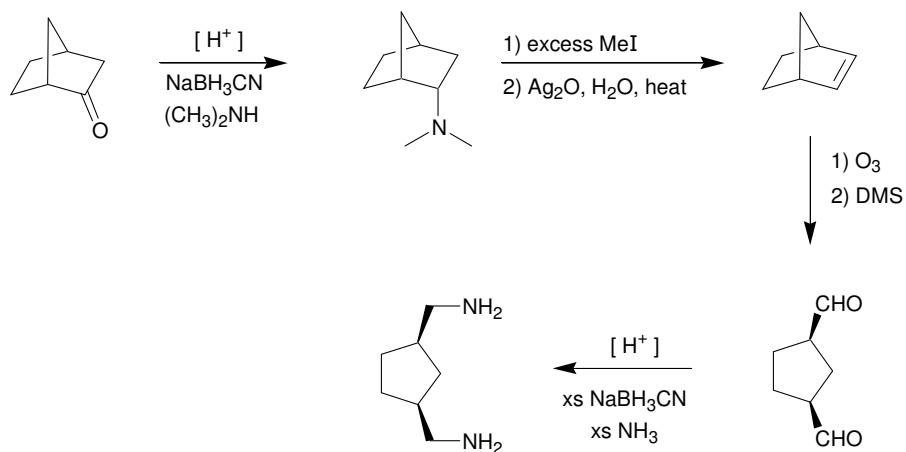


23.61.

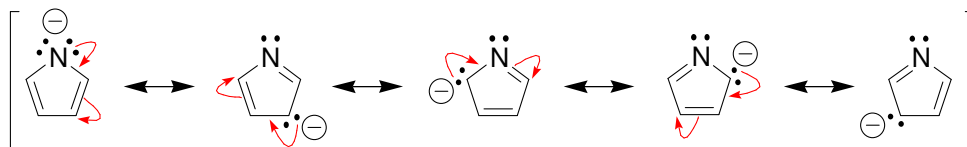
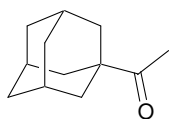


23.62.

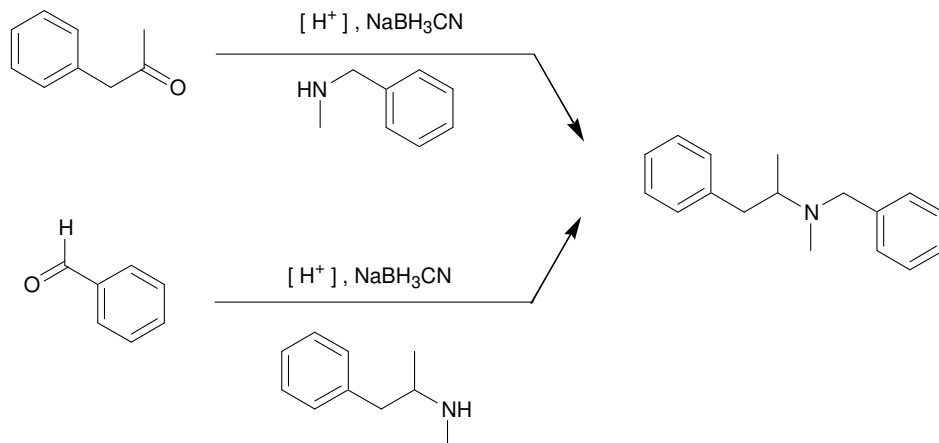


**23.63.**

**23.64.** The conjugate base of pyrrole is highly stabilized because it is an aromatic anion and it is resonance stabilized, spreading the negative charge over all five atoms of the ring:

**23.65.**

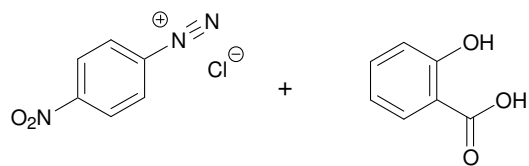
23.66.



23.67.



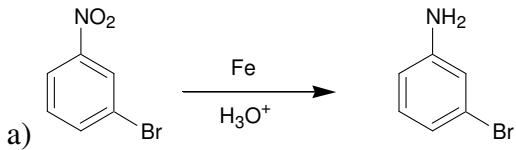
23.68.



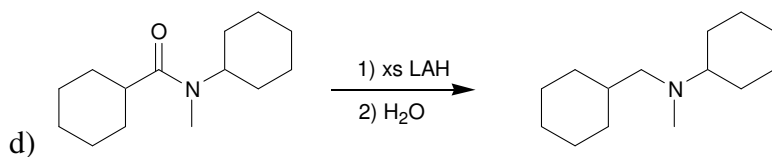
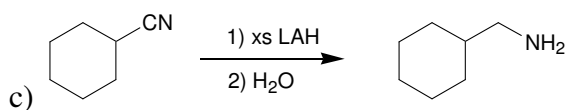
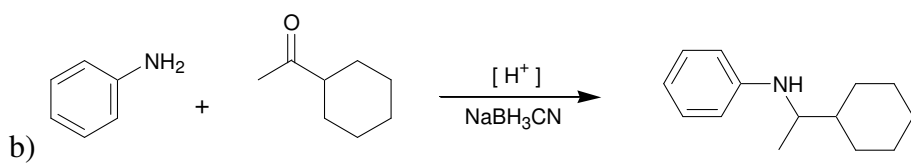
23.69.



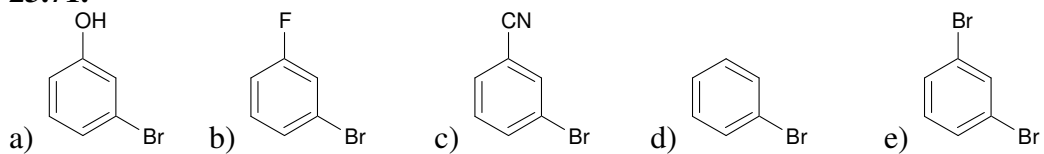
23.70.



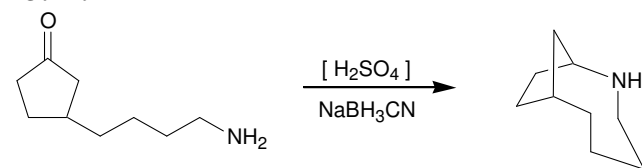




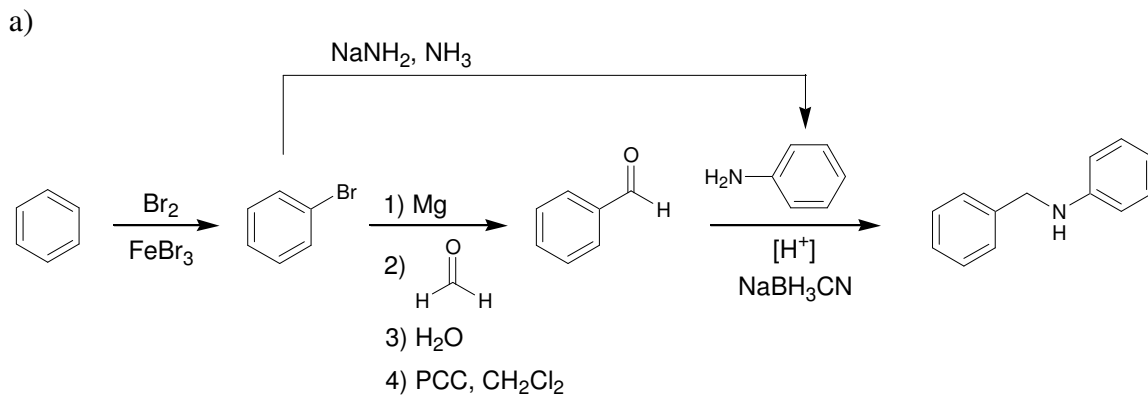
## 23.71.



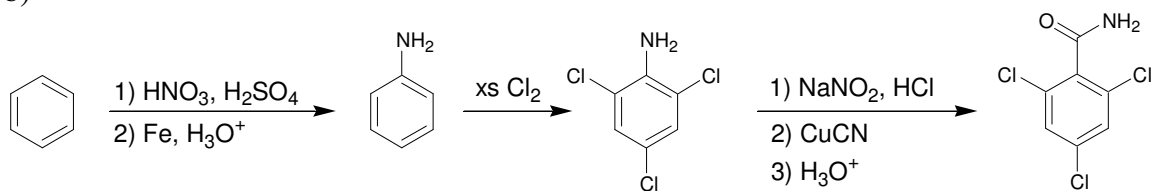
## 23.72.



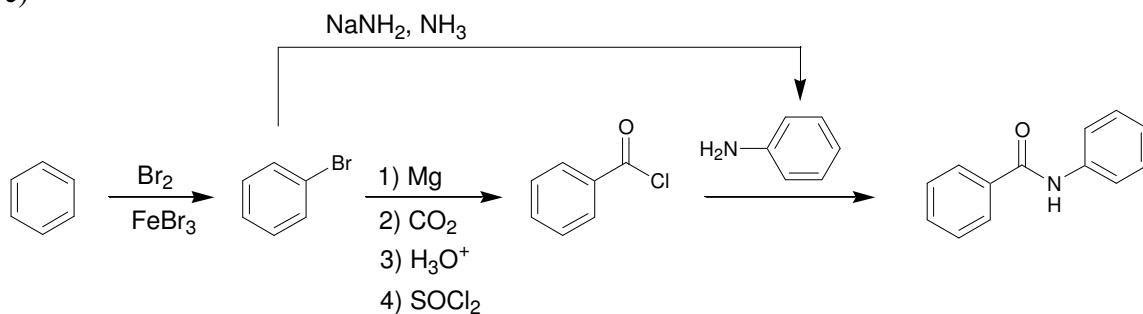
## 23.73.



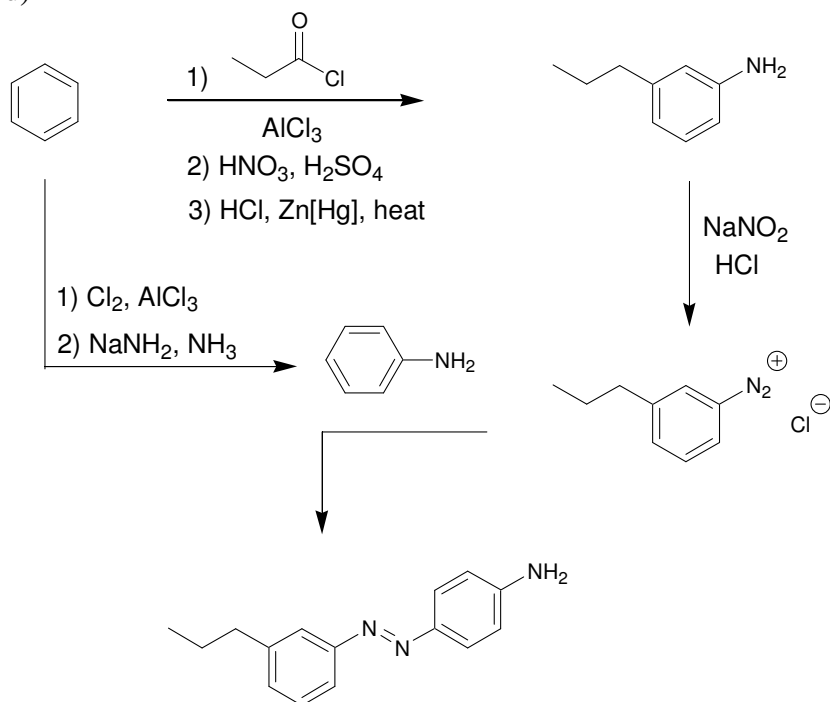
b)



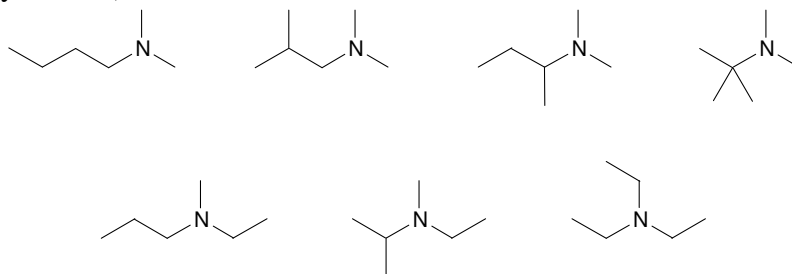
c)



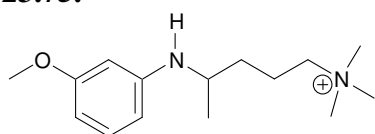
d)



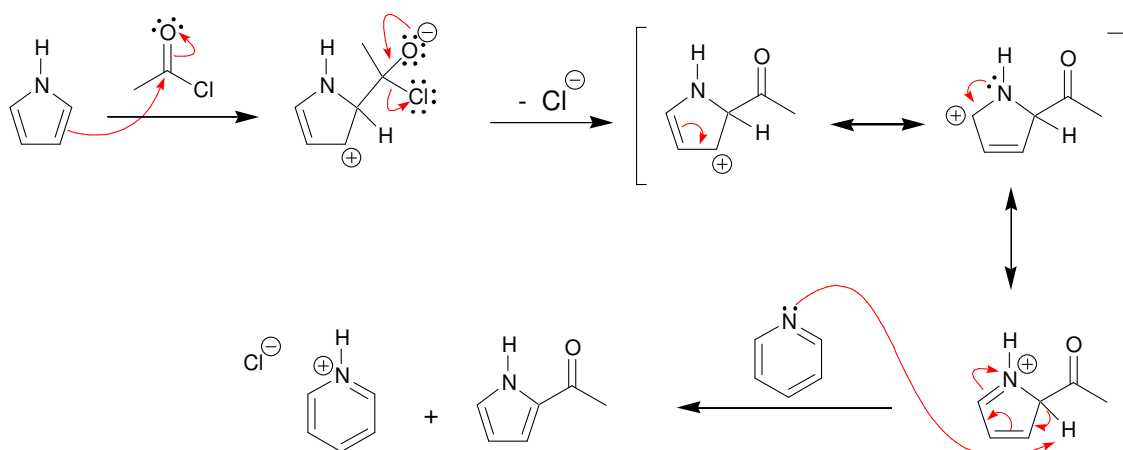
**23.74.** The IR data indicates that we are looking for structures that lack an N-H bond (i.e. tertiary amines):



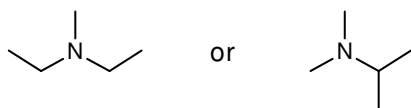
**23.75.**



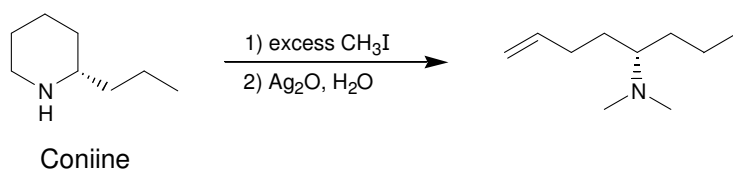
**23.76.**



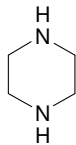
**23.77.** The compound is a tertiary amine with the appropriate symmetry that provides for only three signals:



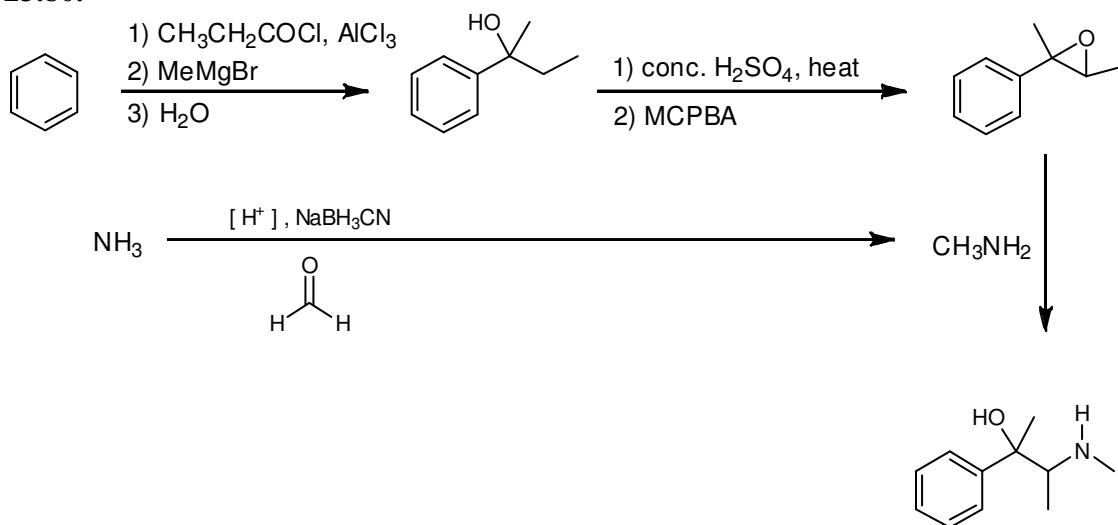
**23.78.**



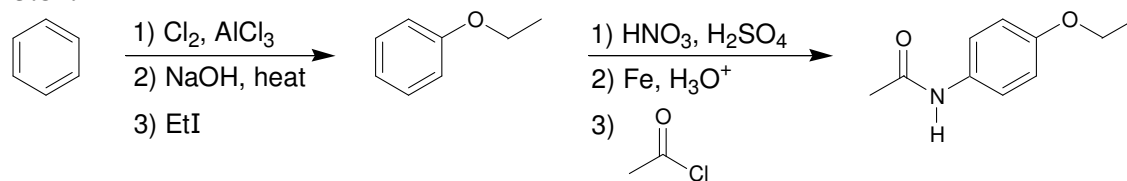
23.79.



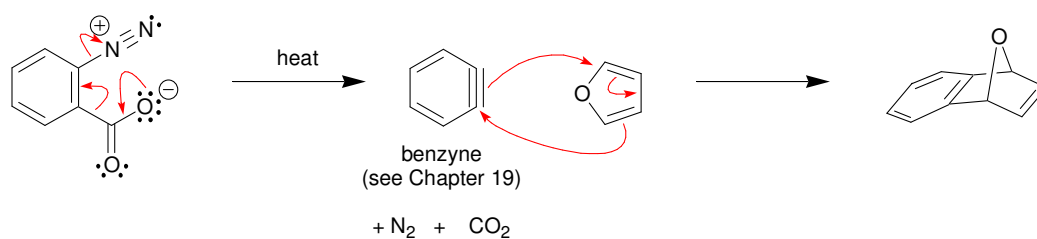
23.80.



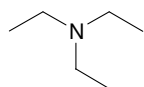
23.81.



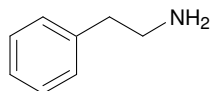
23.82.



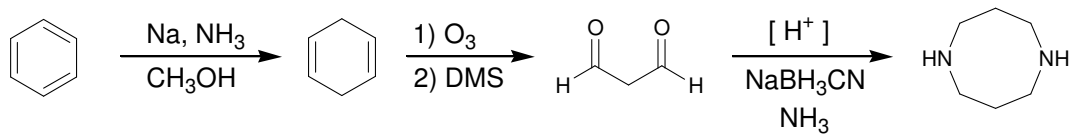
23.83.



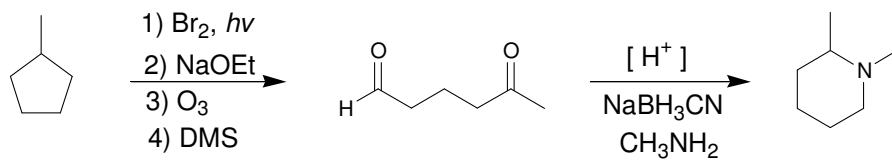
23.84.



23.85.



23.86.





- 23.88.** Protonation of the nitrogen highlighted below results in a cation that is highly resonance stabilized. Protonation of either of the other nitrogen atoms would not result in a resonance stabilized cation:

