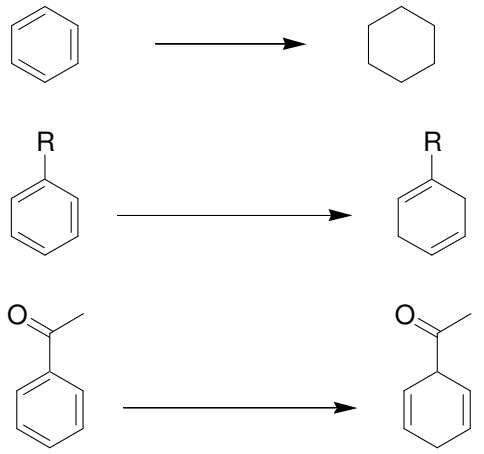


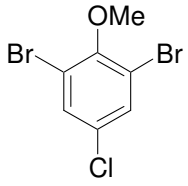
Solutions

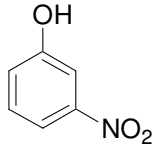
18.1.

a) 3-isopropylbenzaldehyde or *meta*-isopropylbenzaldehyde
b) 2-bromotoluene or *ortho*-bromotoluene
c) 2,4-dinitrophenol
d) 2-ethyl-1,4-diisopropylbenzene
f) 2,6-dibromo-4-chloro-3-ethyl-5-isopropylphenol

18.2.
a) 4-bromo-2-methylphenol
b) 2-hydroxy-5-bromotoluene
c) 4-bromo-1-hydroxy-2-methylbenzene

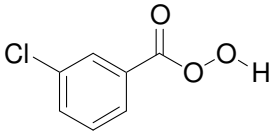
18.3.

a) 

b) 

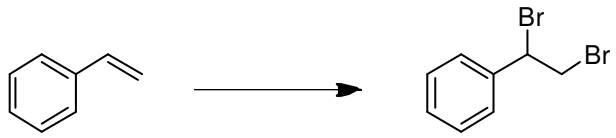
18.4.
a) meta-xylene
b) 1,3-dimethylbenzene
c) meta-dimethylbenzene
d) meta-methyltoluene
e) 3-methyltoluene

18.5.

a) 

b) 3-methylperbenzoic acid or *meta*-methylperbenzoic acid.

18.6.



Compound A (C_8H_8) **Compound B** ($C_8H_8Br_2$)

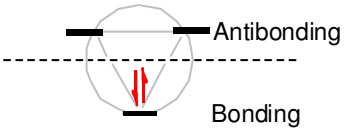
18.7.

a) ΔH has a positive value
b) ΔH has a positive value
c) ΔH has a negative value

18.8.

a) No, 12 is not a Hückel number.
b) Yes, 14 is a Hückel number.
c) No, 16 is not a Hückel number.

18.9. The cyclopropenyl cation is expected to exhibit aromatic stabilization.

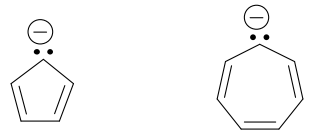


18.10. The compound will be aromatic because there are 22 π electron, and 22 is a Hückel number.

18.11.

a) antiaromatic b) aromatic c) antiaromatic d) aromatic

18.12. Cyclopentadiene is more acidic because its conjugate base is highly stabilized. Deprotonation of cyclopentadiene generates an anion that is aromatic, because it is a continuous system of overlapping p orbitals containing 6 π electrons. In contrast, deprotonation of cycloheptatriene gives an anion with 8 π electrons.

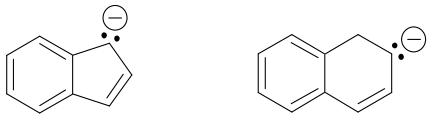


more stable

18.13. The first step of an S_N1 process is loss of a leaving group, forming a carbocation, so we compare the carbocations that would be formed.

The second carbocation is more stable, because it is aromatic, and is therefore lower in energy than the first carbocation. The transition state leading to the second carbocation will be lower in energy than the transition state leading to the first carbocation, and therefore, the second carbocation will be formed more rapidly than the first.

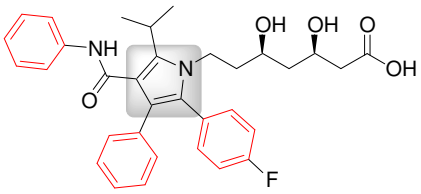
18.14. The first compound is more acidic because deprotonation of the first compound generates a new (second) aromatic ring. Deprotonation of the second compound does not introduce a new aromatic ring:



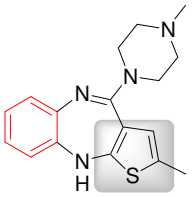
18.15.

a) One of the lone pairs on oxygen
b) One of the lone pairs on sulfur
c) The lone pair on nitrogen is NOT participating in aromaticity (8 pi electrons).
d) One of the lone pairs on sulfur
e) There is only one pair (on oxygen) and it is not participating in aromaticity.
f) Each nitrogen has one lone pair, and neither is participating in aromaticity.
g) The compound is not aromatic. In order to achieve a continuous system of overlapping *p* orbitals, each oxygen atom would need to contribute a lone pair in a *p* orbital, and that would give 8 π electrons (not a Hückel number).
h) One of the lone pairs on oxygen (not the lone pair on the nitrogen)

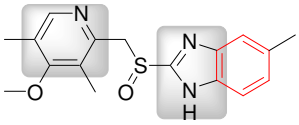
18.16.



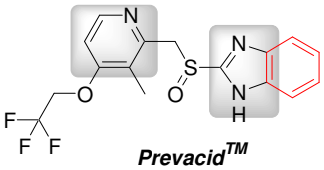
Lipitor™



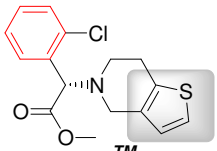
Zyprexa™



Nexium™

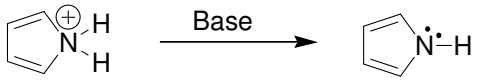


Prevacid™



Plavix™

18.17. The first compound is expected to be more acidic (has a lower pK_a), because deprotonation restores aromaticity to the ring. The second compound is already aromatic, even before deprotonation.



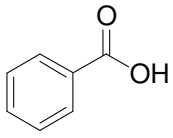
not aromatic **aromatic**

18.18.

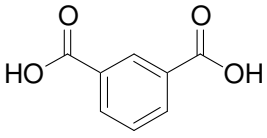
a) Yes, it has the required pharmacophore (two aromatic rings separated by one carbon atom, and a tertiary amine.
b) Meclizine crosses the blood-brain barrier and binds with receptors in the central nervous system, causing sedation.
c) Introduce polar functional groups that reduce the ability of the compound to cross the blood-brain barrier.

18.19.

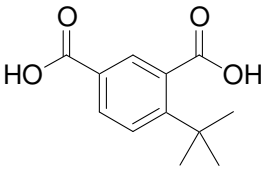
a)



b)

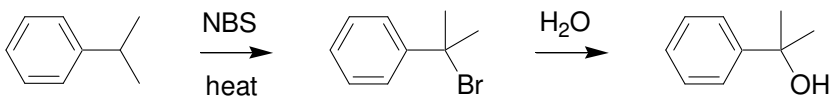


c)

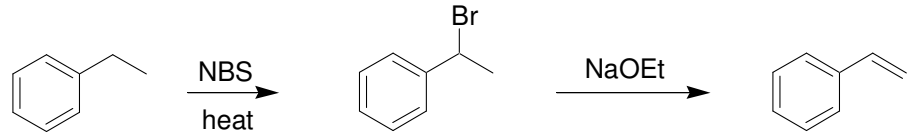


18.20.

a)



b)



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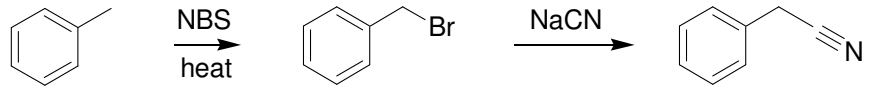
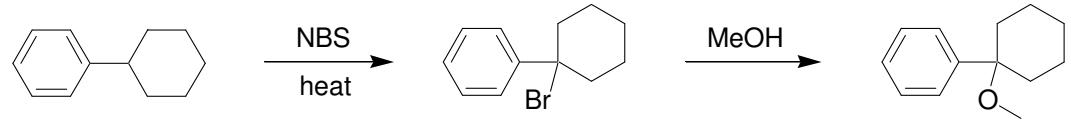
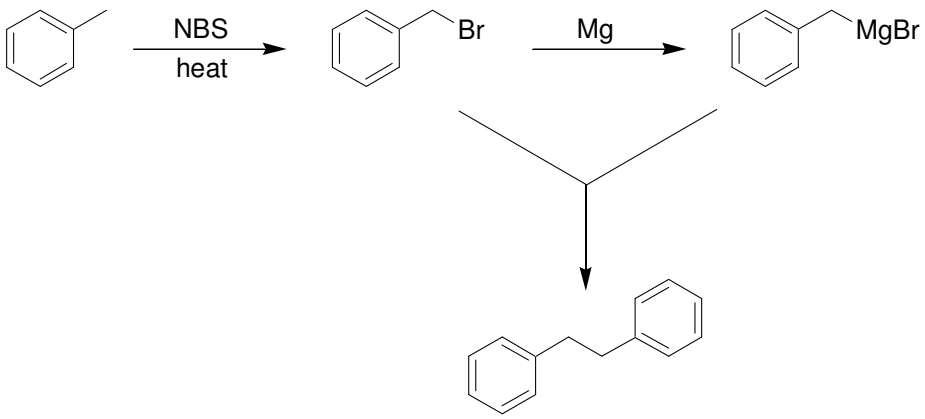


d)



18.21.



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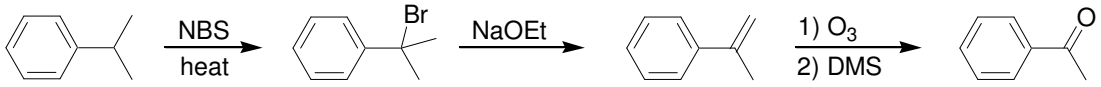
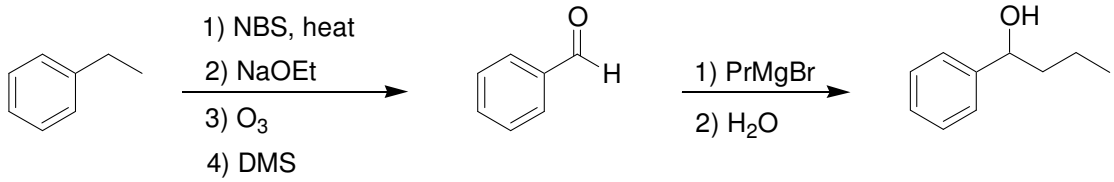
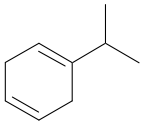
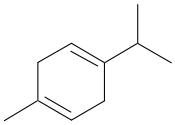
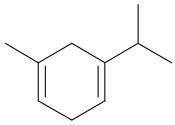
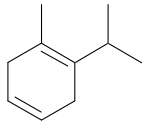
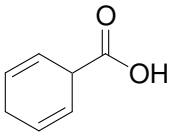
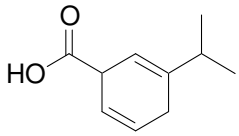


18.23.

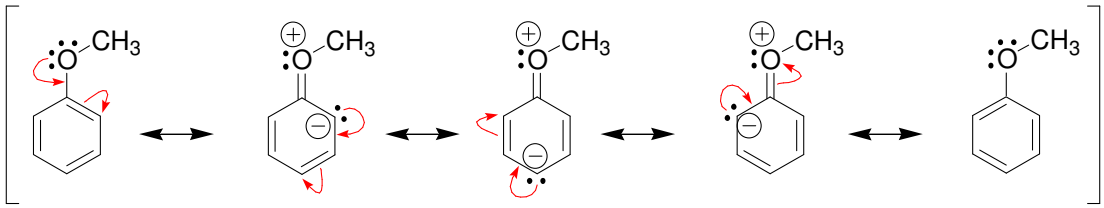


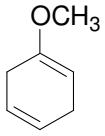
18.24.

a)  b)  c)  d) 

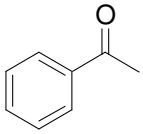
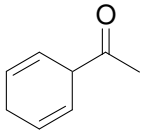
e)  f) 

18.25.

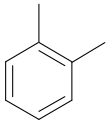
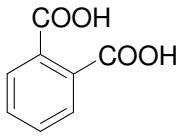
a) 

b) 

18.26.

a)  b) acetophenone c) 

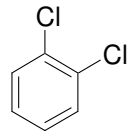
18.27.

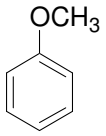
a)  b) *ortho*-xylene c) 

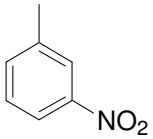
18.28.

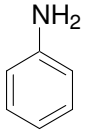
a) 4-ethylbenzoic acid or *para*-ethylbenzoic acid
b) 2-bromophenol or *ortho*-bromophenol
c) 2-chloro-4-nitrophenol
d) 2-bromo-5-nitrobenzaldehyde
e) 1,4-diisopropyl benzene or *para*-diisopropyl benzene

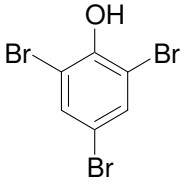
18.29.

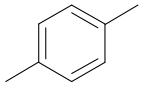
a) 

b) 

c) 

d) 

e) 

f) 

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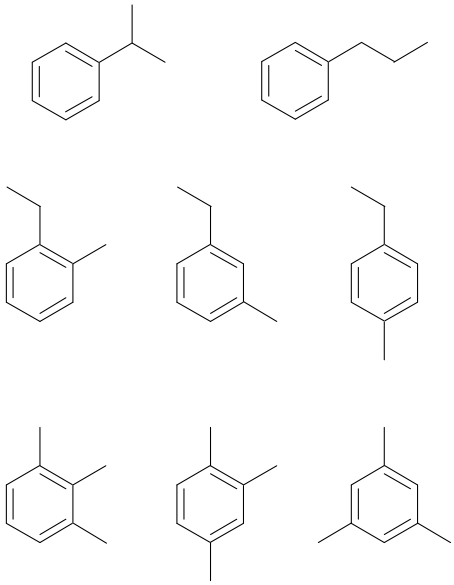

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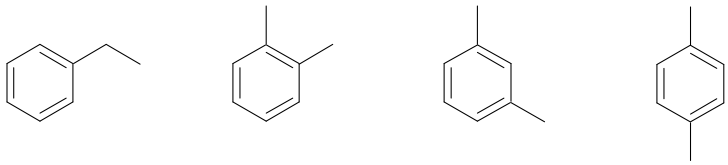

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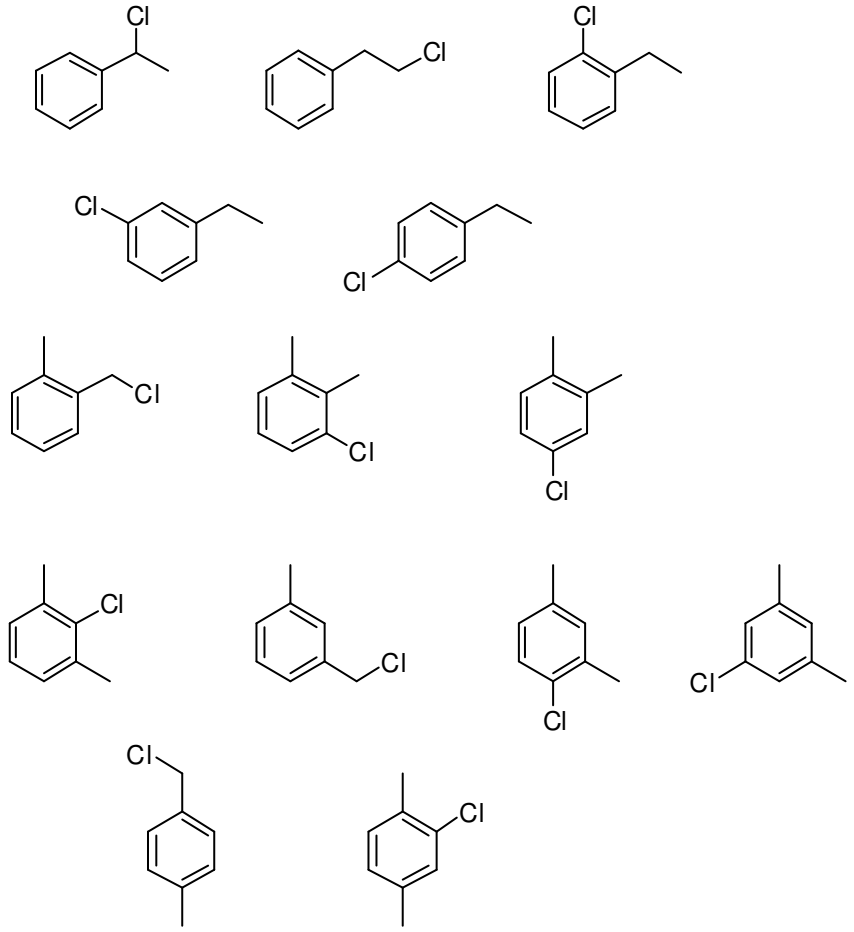

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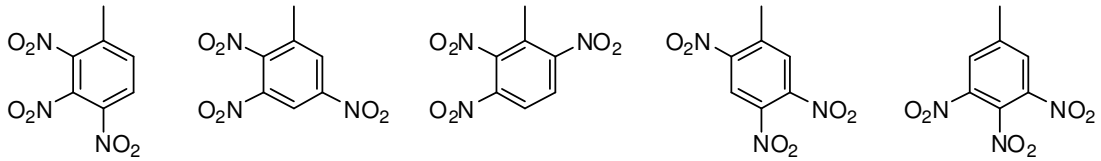


2,3,4-trinitrotoluene | 2,3,5-trinitrotoluene | 2,3,6-trinitrotoluene | 2,4,5-trinitrotoluene | 3,4,5-trinitrotoluene

18.34.

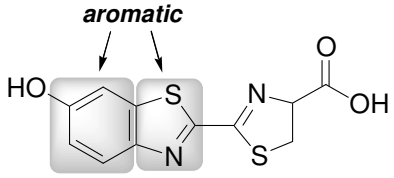
a) 10 b) 6 c) 10 d) 4 e) 6

18.35.

a) benzene b) benzene c) benzene
d) cyclohexane e) benzene f) cyclohexane
g) benzene h) benzene i) benzene
j) cyclohexane k) cyclohexane

18.36. a) Yes b) No c) No d) Yes e) No

18.37.

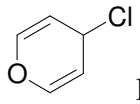
a) 

b) One of the lone pairs on the sulfur atom in the five-membered aromatic ring

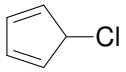
18.38.

a) Nonaromatic. The lone pairs on the oxygen atom will remain in sp^3 hybridized orbitals in order to avoid anti-aromaticity.
b) Nonaromatic. The lone pair on the nitrogen atom will remain in an sp^3 hybridized orbital in order to avoid anti-aromaticity.
c) Aromatic. One of the lone pairs of the sulfur atom occupies a *p* orbital, thereby establishing a continuous system of overlapping *p* orbitals, containing six π electrons.
d) Aromatic. Both lone pairs occupy sp^2 hybridized orbitals and do not participate in establishing aromaticity.
e) Aromatic. A continuous system of overlapping *p* orbitals, containing six π electrons.
f) Non aromatic. The nitrogen atom does not have a *p* orbital, so there is not a continuous system of overlapping *p* orbitals.
g) Aromatic. The lone pair of the oxygen atom occupies a *p* orbital, thereby establishing a continuous system of overlapping *p* orbitals, containing six π electrons.
h) Aromatic. Both lone pairs occupy *p* orbitals, thereby establishing a continuous system of overlapping *p* orbitals, containing six π electrons.

18.39.

a) 

Loss of the leaving group generates an aromatic cation.

b) 

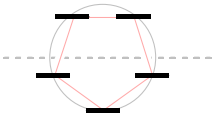
Loss of the leaving group generates an antiaromatic cation.

18.40.


Deprotonation of cyclopentadiene generates an aromatic anion.

18.41. The second compound is a stronger base, because the lone pair on the nitrogen atom is localized and available to function as a base. However, the nitrogen atom in the first compound is delocalized and is participating in aromaticity. This lone pair is unavailable to function as a base, because that would cause a loss of aromaticity.

18.42. Six π electrons are required in order to achieve aromaticity. This cation only has four electrons.



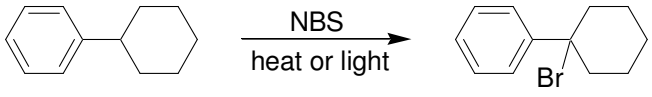
18.43. If both lone pairs occupy *p* orbitals, then there is a continuous system of overlapping *p* orbitals. There are 10 π electrons, so the dianion is aromatic.

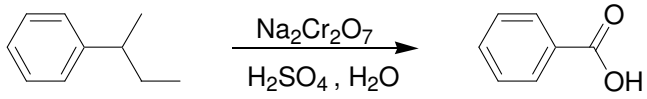
18.44. Yes. The lone pairs on the nitrogen atoms do not contribute to aromaticity. They occupy sp^2 hybridized orbitals. One of the lone pairs on the oxygen atom (in the ring) occupies a *p* orbital, giving a continuous system of overlapping *p* orbitals containing six π electrons.

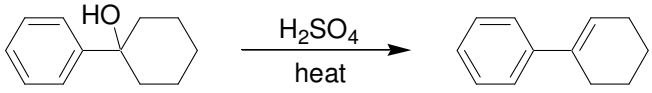
18.45. Steric hindrance forces the rings out of coplanarity.

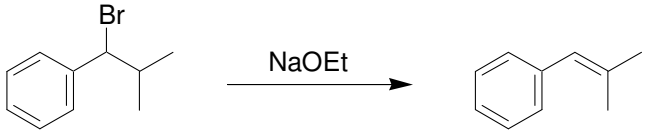
18.46. Benzene does not have three C-C single bond and three C-C double bonds. In fact, all six C-C bonds of the ring have the same bond order are the same length. However, cyclooctatetraene has four isolated π bonds. The molecule adopts a tub shape to avoid antiaromaticity. Some of the C-C bonds are double bonds (shorter in length), and some of the C-C bonds are single bonds (longer in length). Therefore, the two methyl groups can be separated by a C-C single bond or a C=C double bond. And those two possibilities represent different compounds.

18.47.

a) 

b) 

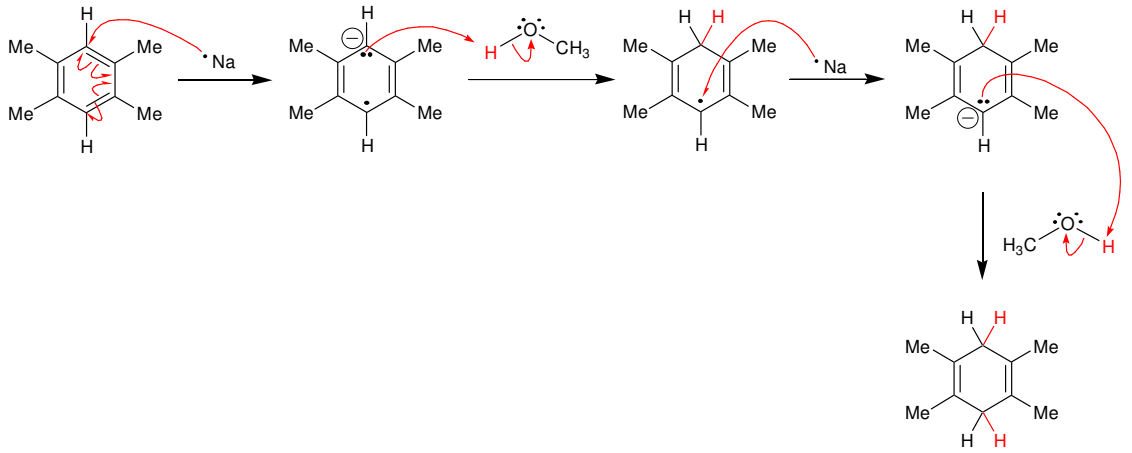
c) 

d) 

18.48.

a) 6 b) 5 c) 3 d) 9

18.49.



18.50. *meta*-Xylene.

18.51.

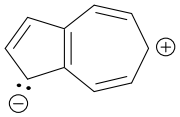
a) The first compound would lack C-H stretching signals just above 3000 cm^{-1}, while the second compound will have C-H stretching signals just above 3000 cm^{-1}.
b) The ^{1}H NMR spectrum of the first compound will have only one signal, while the ^{1}H NMR spectrum of the second compound will have two signals.
c) The ^{13}C NMR spectrum of the first compound will have only two signals, while the ^{13}C NMR spectrum of the second compound will have three signals.

18.52. When either compound is deprotonated, an aromatic anion is generated, which can be drawn with five resonance structures. The resulting anion is the same in either case.

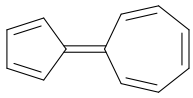
18.53. In cycloheptatrienone, the resonance structures with C+ and O- contribute significant character to the overall resonance hybrid, because these forms are aromatic. Therefore, the oxygen atom of this C=O bond is particularly electron rich. A similar analysis of cyclopentadienone reveals resonance structures with antiaromatic character. These resonance structures contribute very little character to the overall resonance hybrid, and as a result, the oxygen atom of this C=O bond is not as electron rich when compared with most C=O bonds.

18.54.

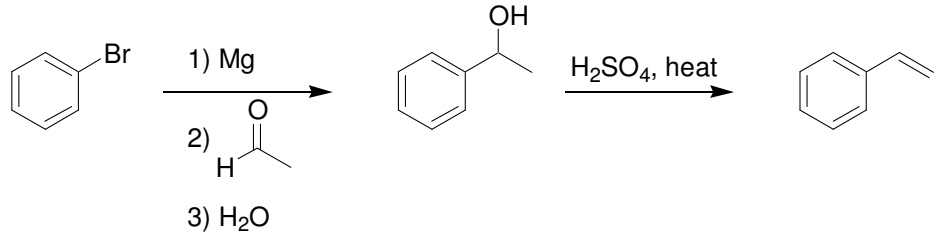
a) Each of the rings in the following resonance structure is aromatic.



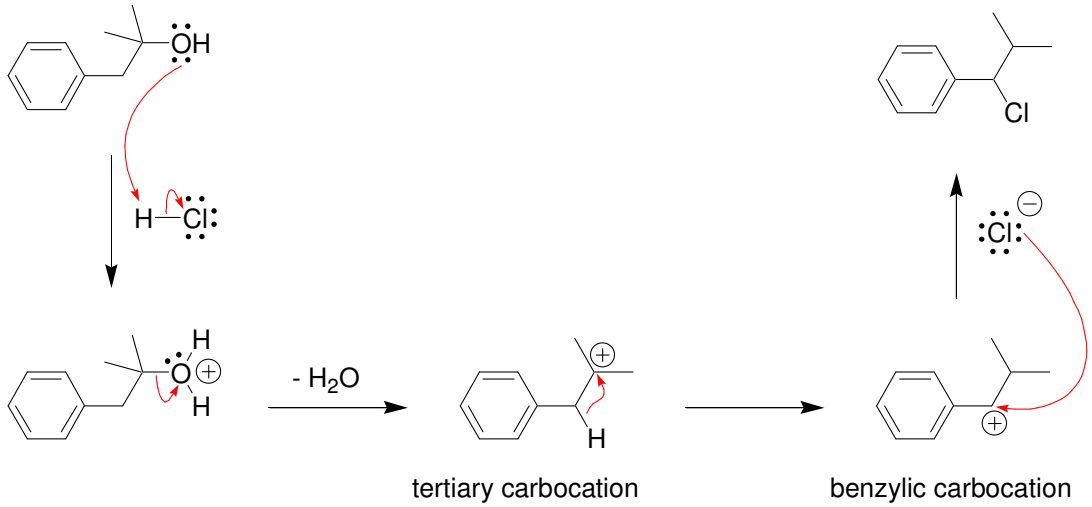
Therefore, this resonance structure contributes significant character to the overall resonance hybrid, which gives the azulene a considerable dipole moment.

b) 

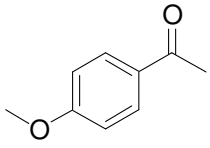
18.55.



18.56.

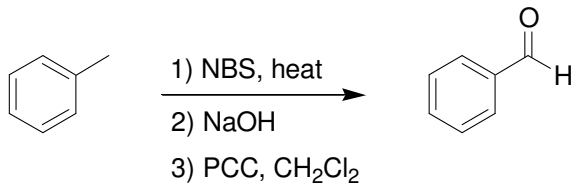


18.57.



18.58.

a)



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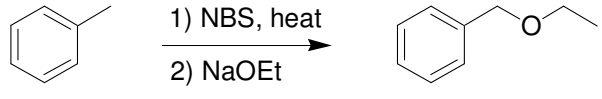
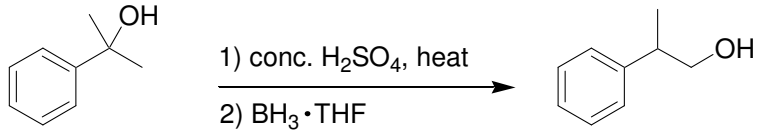


c)



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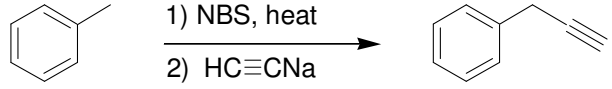
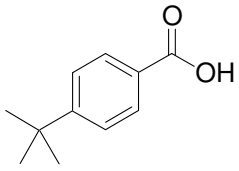
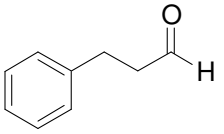


18.59.



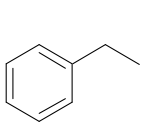
18.60.



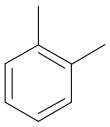
18.61.
a) The second compound holds greater promise as a potential antihistamine, because it possesses two planar aromatic rings separated from each other by one carbon atom. The first compound has only one aromatic ring. The ring with sulfur and oxygen is not aromatic and not planar.
b) Yes, because it lacks polar functional groups that would prevent it from crossing the blood-brain barrier.

18.62. No, this compound possesses an allene moiety (C=C=C). The *p* orbitals of one C=C bond of the allene moiety do not overlap with the *p* orbitals of the other C=C bond. This prevents the compound from having one continuous system of overlapping *p* orbitals.

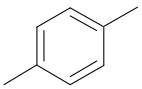
18.63.



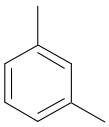
Compound A



Compound B



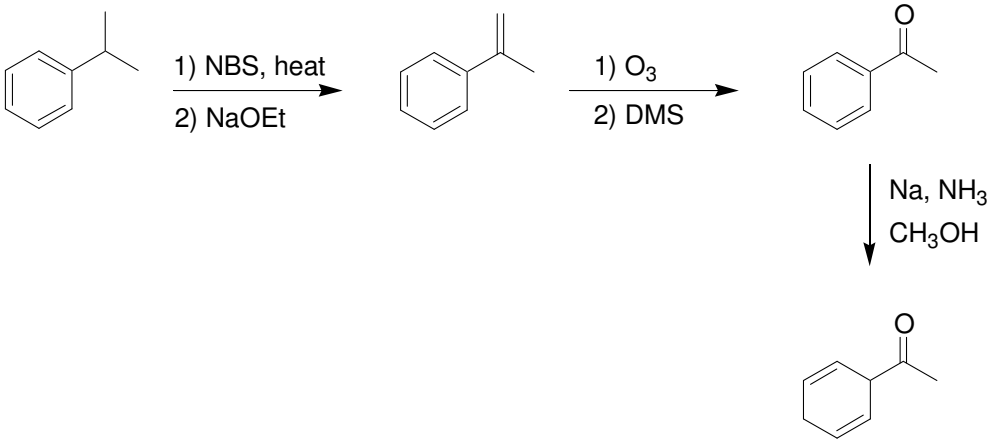
Compound C



Compound D

18.64. The nitrogen atom in compound A is localized and is not participating in resonance. The nitrogen atom in compound B is delocalized, and some of the resonance structures are aromatic. These resonance structures contribute significant character to the overall resonance hybrid. The nitrogen atom in compound B is not available to function as a base.

18.65.



18.66.