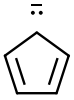
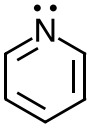
Objective 6 Quiz Practice Problem solutions

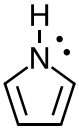
1. a. Cyclopentadiene is not aromatic but the cyclopentadiene anion is aromatic. Apply the aromaticity rules to each compound.

b. Pyridine (it stinks) is aromatic. The N on pyridine is trigonal planar and is sp^2 hybridized. The lone pair on N is not part of the conjugated pi system. This means the lone pair occupies the ____ orbital and the pi bond occupies the _____ orbital. (Choices: sp^2 hybrid orbital or p orbital)

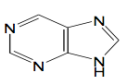


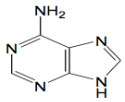
c. The N on pyrrole is sp^2 hybridized. Pyrrole has a lone pair on the N. This lone pair is part of the conjugated pi system. Is pyrrole aromatic?

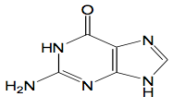


d. The furan ring is aromatic. Is each lone pair on the O part of the conjugated pi system?

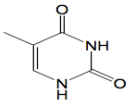
e. DNA bases are aromatic. How many pi electrons does each base have? Are the lone pairs on N part of the conjugated pi system?

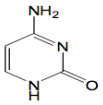

Purine


Adenine


Guanine


Pyrimidine


Thymine


Cytosine

Answers:

a. Cyclopentadiene is not aromatic.

Ring = yes

Conjugated = no. 4 carbons is conjugated pi electron system but not 5th carbon.

Planar = no. C with 4 single bonds is tetrahedral.

4n + 2 pi electrons = no. Cyclopentadiene has 4 electrons, not 2 or 6 or 10 etc.

Cyclopentadiene anion is aromatic

Ring = yes

Conjugated = yes. Lone pair is part of conjugated pi electron system.

Planar = yes. C with lone pair and negative charge is trigonal planar, sp^2 hybridized with lone pair in p orbital and part of conjugated pi electron system.

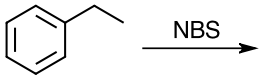
4n + 2 pi electrons = yes. Cyclopentadiene has 6 electrons in conjugated pi electron system (4 from pi bonds and 2 from lone pair).

b. Pyridine (it stinks) is aromatic.The N on pyridine is trigonal planar and is sp^2 hybridized. The lone pair on N is not part of the conjugated pi system. This means the lone pair occupies the sp^2 hybrid orbital and the pi bond occupies the p orbital. (Choices: sp^2 hybrid orbital or p orbital)

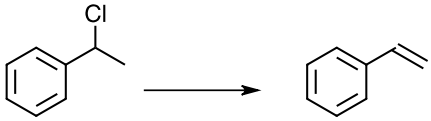
Ring = yes

Conjugated = yes
Planar = yes. N on pyridine is trigonal planar and is sp^2 hybridized.
4n + 2 pi electrons = yes. Pyridine has 6 pi electrons. Lone pair on N is not part of conjugated pi electrons.
c. Pyrrole is aromatic.
Ring = yes
Conjugated = yes. Lone pair is part of conjugated pi electron system.
Planar = yes. N with lone pair is trigonal planar, sp^2 hybridized with lone pair in sp^2 hybrid orbital and not part of conjugated pi electron system.
4n + 2 pi electrons = yes. Pyrrole has 6 electrons in conjugated pi electron system (4 from pi bonds and 2 from lone pair).
d. The furan ring is aromatic. One lone pair on the O is part of the conjugated pi system (4 from pi bonds and 2 from lone pair) and occupies a p orbital. The 2nd lone pair occupies a sp^2 hybrid orbital and is not part of the conjugated pi system.
e. DNA bases
Purine has 10 electrons in the conjugated pi system. The lone pair on the N bonded to the H (bottom right) is part of the conjugated pi electron system.
Adenine has 10 electrons in the conjugated pi system. The lone pair on the N bonded to the H (bottom right) is part of the conjugated pi electron system.
Guanine has 10 electrons in the conjugated pi system. The lone pair on each N bonded to the H (upper left and bottom right) in the ring is part of the conjugated pi electron system.
Pyrmidine has 6 electrons in the conjugated pi system. The lone pairs on each N are not part of the conjugated pi system.
Thymine has 6 electrons in the conjugated pi system. The lone pair on each N is part of the conjugated pi electron system.
Cytosine has 6 electrons in the conjugated pi system. The lone pair on the N bonded to the H in the ring is part of the conjugated pi electron system. The lone pair on the other N in the ring is not part of the conjugated pi electron system.

2. Reactions on arene side chain.
a. NBS is a special brominating agent in which Br substitutes for H at the allylic C. Identify the allylic C. Then, draw the structure of the product.

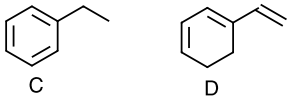


b. Consider the reaction. What is the reaction type? The Cl behaves like a _____. What reagent would you use? Use curved arrows to show how reactant forms product.



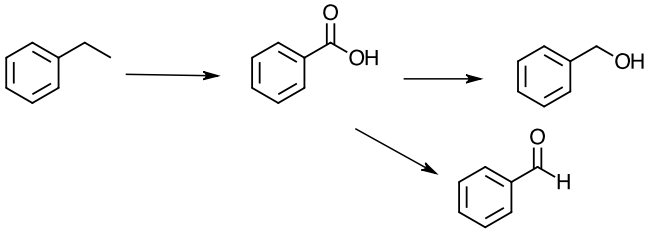
A B

c. Which pi bond in the Structure B is more reactive? Why?
d. What reagent would you use to convert Structure B back to Structure A? Use curved arrows to show how this reaction occurs.
e. Which product forms when Structure B reacts with H_2/Pd? Why?



C D

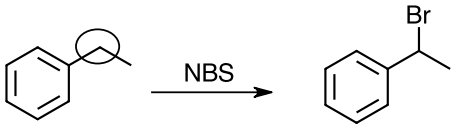
f. Classify each reaction as an oxidation or reduction reaction. What reagent would you use in each reaction?



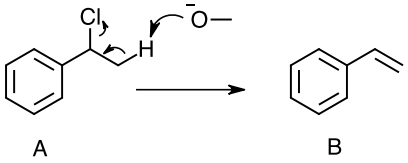
g. The following reaction has been described in the chemical literature and gives a single organic product in good yield. What is the HDI of $C_{12}H_{14}$? Identify the product.

Answers:

a. Circled C is the allylic carbon. An allylic carbon that is adjacent to an aromatic ring is also called a “benzylic” carbon.

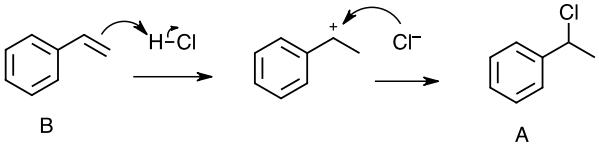


b. Reaction type = elimination reaction. The Cl behaves like a leaving group. Reagent to use = strong base (nucleophile) on 2° RCl, e.g., CH_3O^-.

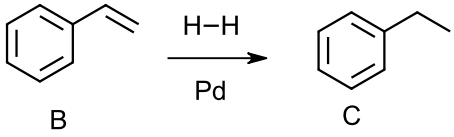


c. In Structure B, the pi bond in the side chain is more reactive because the pi electrons are localized between the 2 carbon atoms whereas the pi bonds in the aromatic ring are delocalized between the 6 carbons in the ring. The pi bond in the side chain is less stable and more reactive; the pi bonds in the ring are more stable and less reactive. See Reactivity Principles and Trends Table.

d. To convert Structure B back to Structure A, use HCl in an addition reaction.

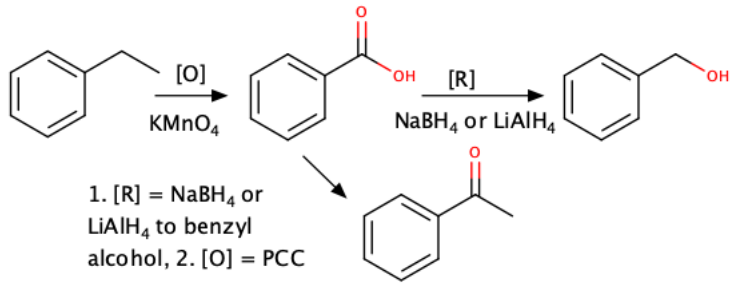


e. The the pi bond in the side chain is more reactive than the pi bonds in the aromatic ring. See Question 2b.



f. [O] = oxidation, [R] = reduction

Benzoic acid to acetophenone is a reduction reaction but it can’t be done in one step because a reducing agent like NaBH4 or LiAlH4 reduces the acid group in benzoic acid to an alcohol. So, 2 steps are needed: reduce benzoic acid to benzyl alcohol and then oxidize benzyl alcohol to acetophenone.



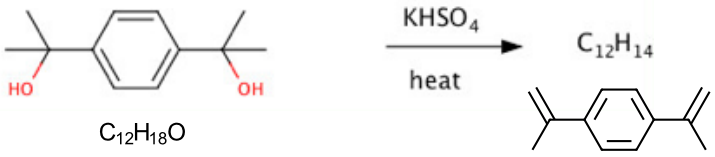
g. HDI of $C_{12}H_{14}$ = 0.5 (26 -14) = 6 --> 6 pi bonds or 6 rings or combination of 6 pi bonds and rings.

Fully saturated 12 carbon alkane = $C_{12}H_{26}$.

$KHSO_4$ = ignore K^+, HSO_4^- = is an acid or base.

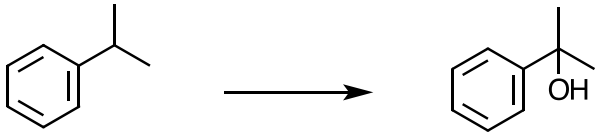
Make OH into a better leaving group with HSO_4^-.

Then, SO_4^{-2} reacts at H on beta C to form C=C bond in an elimination reaction.

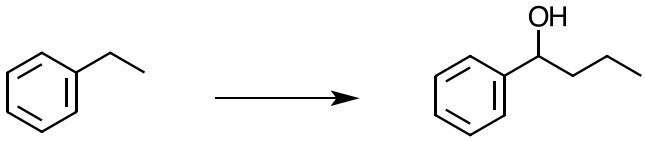


3. Describe a synthesis.

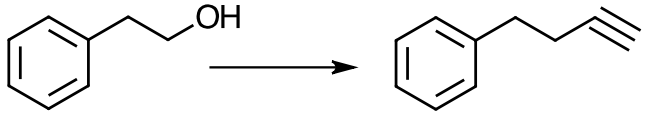
a. How many carbons are in the starting material and target compound? What is the reaction type? At what position is something happening? Does a C-C bond have to form? If so, what method would you use (acetylide, Grignard)?



b. How many carbons are in the starting material and target compound? What is the reaction type? At what position is something happening? Does a C-C bond have to form? If so, what method would you use (acetylide, Grignard)?

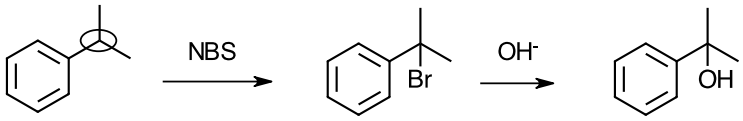


c. How many carbons are in the starting material and target compound? What is the reaction type? At what position is something happening? Does a C-C bond have to form? If so, what method would you use (acetylide, Grignard)?

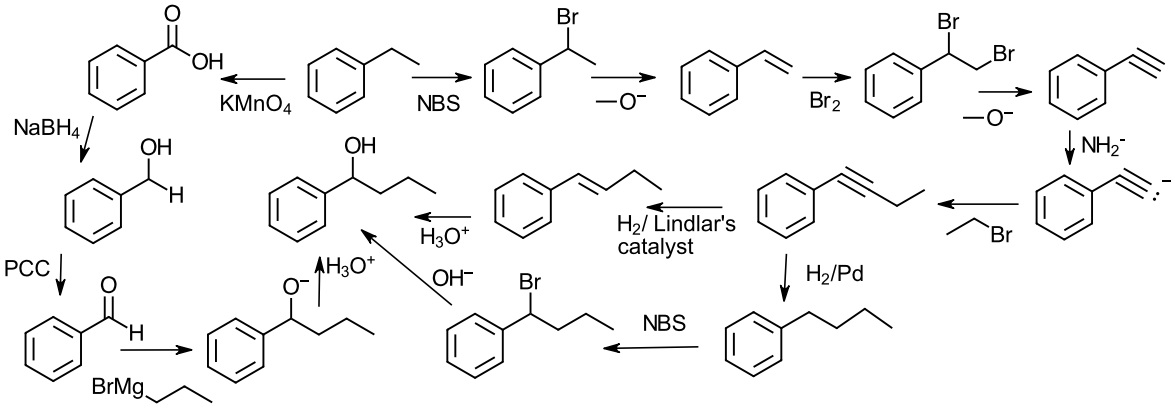


Answer:

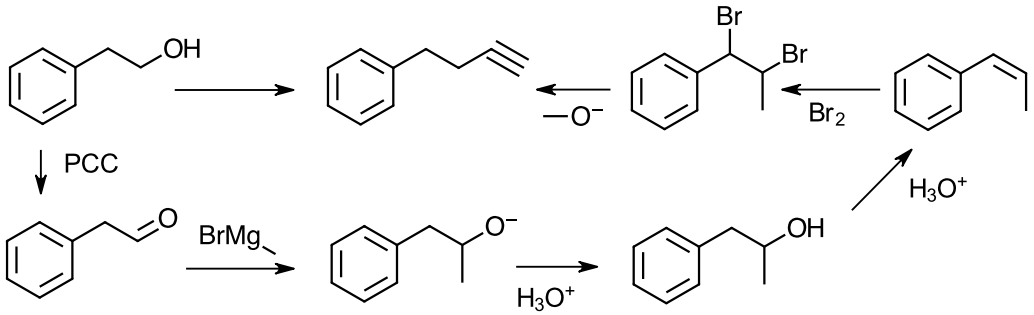
a. Note: the OH group in the product is on the benzylic carbon. Benzylic C is a type of allylic carbon.
Circled C in reactant is the benzylic carbon.



b. 8 carbon reactant --> 10 carbon product. Have to make a C-C bond.
10 carbon product has OH group on benzylic carbon.
Use acetylide ion to make C-C bond = 8 or 9 step synthesis.
Use Grignard reagent (RMgBr) = 5 step synthesis.



c. 8 carbon reactant --> 9 carbon product. Have to make a C-C bond.


OH
PCC
O
BrMg
O⁻
H₃O⁺
OH
H₃O⁺
—O⁻
Br
Br
Br₂