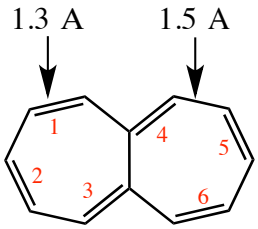
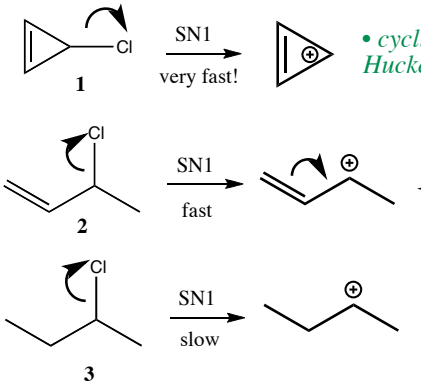
Chapter 18 Practice Problems
Solutions

1



• Compound **1** has 6 C=C bonds similar to the one in cycloheptene
• A simple calculation of 6 x 118 = 708 kJ/mol provides a baseline heat of hydrogenation. If compound **1**'s heat of hydrogenation is close to 708, it would be non-aromatic. If it was much lower than 708, it would be aromatic, and if it was much higher than 708, it would be anti-aromatic.
• The experimental heat of hydrogenation for compound **1** is 790 = 82 kJ/mol which is much higher than predicted (i.e. much LESS stable than predicted). Thus, this compound would be considered to be anti-aromatic!
• Note that this is consistent with the 12 pi electron system (a 4n number)
• The bonds would alternate between a single C-C bond length and a double C=C bond length as shown.

2



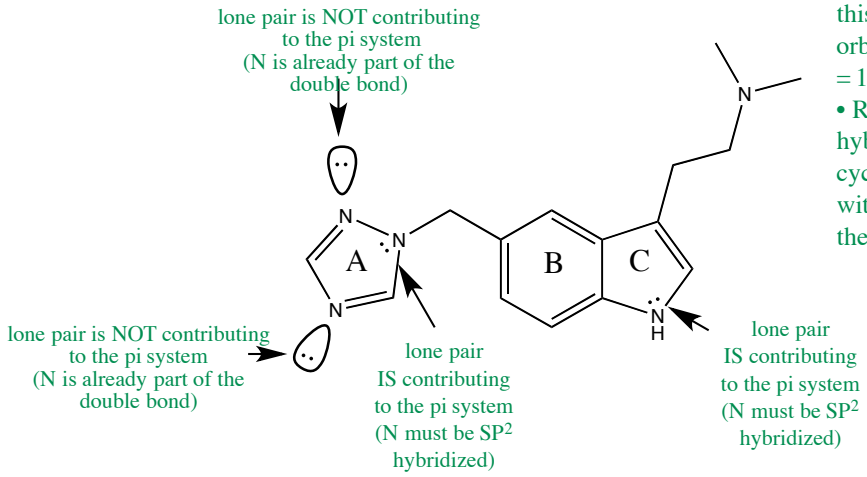
• *cyclic array of SP2 hybridized orbitals with 2 pi electrons (a 4n+2 Huckel number where n = 0) = aromatic!*

• *resonance stabilized 2° allylic carbocation*

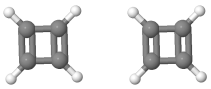
• *just a 2° carbocation*

• The rate determining step for an S_N1 reaction is formation of the intermediate carbocation
• Therefore, we need only consider the relative stabilities of the carbocations that would be formed upon loss of the leaving group in each case to determine why one is faster than the other. A faster reaction MUST have a more stable carbocation intermediate!
• 2 is faster than 3 because the 2° allylic carbocation formed is more stable than the 2° carbocation
• 1 is faster than 2 because the carbocation formed from 1 is aromatic!

3

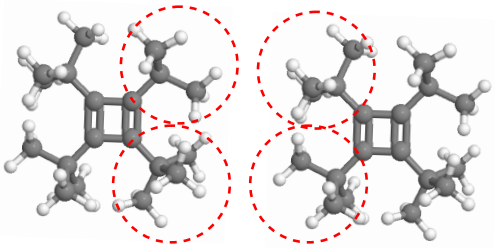


• Ring A: with the N atom SP^2 hybridized, this is a cyclic array of SP^2 hybridized orbitals with 6 pi electrons (4n+2 where n = 1) in the ring system = aromatic!
• Rings B,C: with the N atom SP^2 hybridized, the two fused rings form a cyclic array of SP^2 hybridized orbitals with 10 pi electrons (4n+ 2 where n = 2) in the ring system = aromatic!



• these two small molecules have no problem getting close enough to each other to react with each other (dimerize)

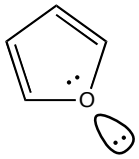
4



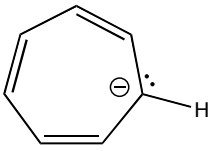
• however, adding tert-butyl groups to the rings creates a large of amount of steric interference that prevents the two molecules from approaching one another, preventing the dimerization!

5

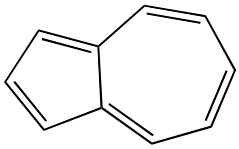
6 pi electrons: YES!



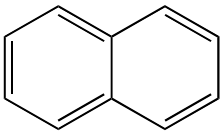
if carbon was SP^2 hybridized there would be 8 pi electrons: NO!



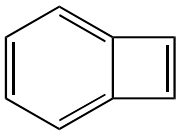
10 pi electrons: YES!



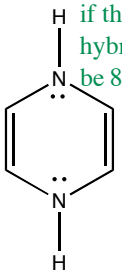
10 pi electrons: YES!



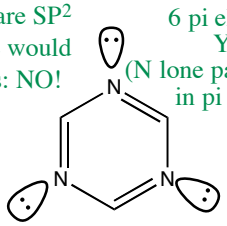
8 pi electrons: NO!



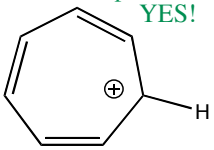
if the nitrogens are SP^2 hybridized there would be 8 pi electrons: NO!



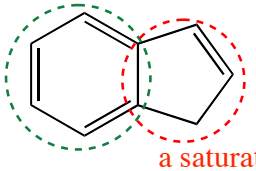
6 pi electrons: YES! (N lone pairs are NOT in pi system)



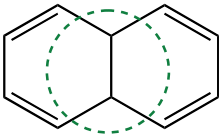
6 pi electrons: YES!



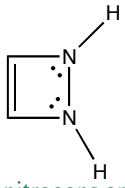
6 pi electrons in this ring: YES!



a saturated CH_2 in this ring: NO!

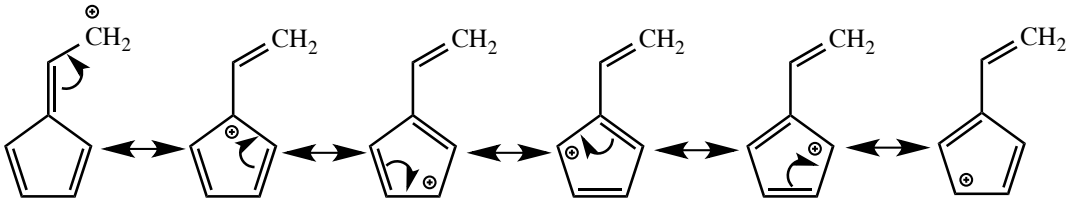


saturated CH_2's in both rings: NO!



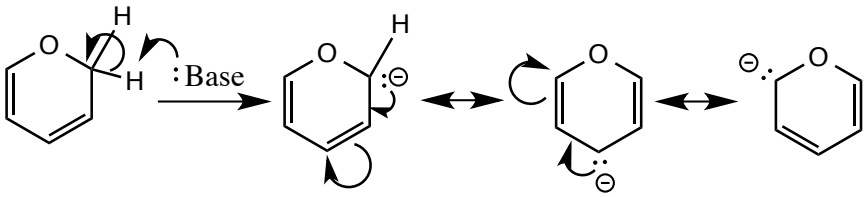
if the nitrogens are SP^2 hybridized there would be 6 pi electrons: YES!

6

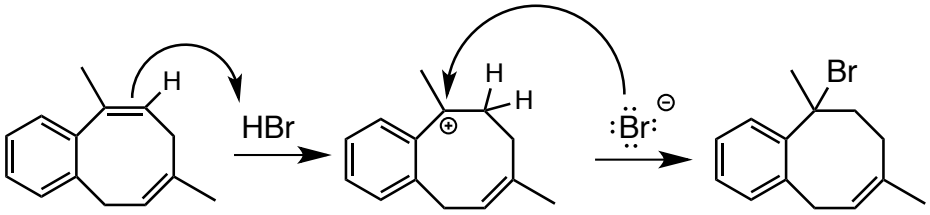


• *any others are duplicates or incorrect!*

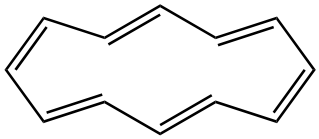
7



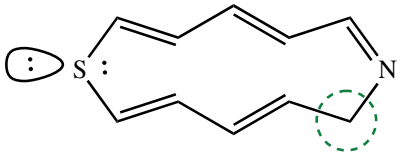
8



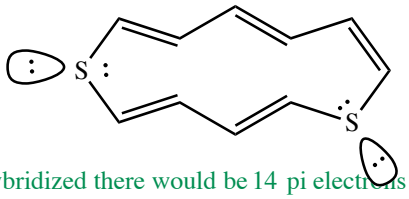
3° benzylic carbocation
is the most stable possible
intermediate that can be
formed upon protonation by HBr



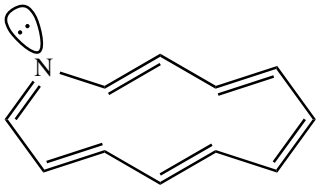
12 pi electrons:
NO!



saturated CH_2 in the ring: NO!

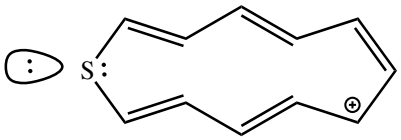


if both S atoms are SP^2 hybridized there would be 14 pi electrons (4n+2 where n = 3):
YES!

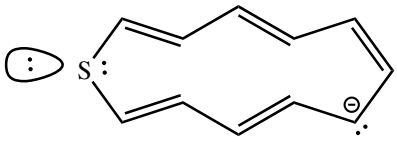


12 pi electrons:
NO!

9



if the S atoms is SP^2 hybridized there would be 12 pi electrons:
NO!



if the S and C^- atoms are both SP^2 hybridized
there would be 14 pi electrons (4n+2 where n = 3):
YES!