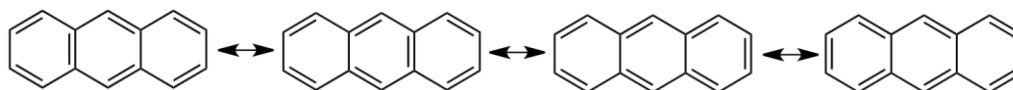


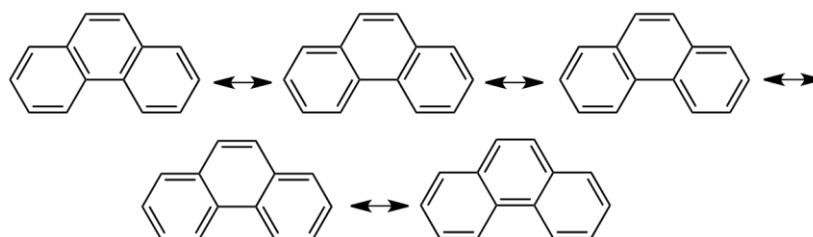
Solutions to Exercises, Chapter 19

19.1

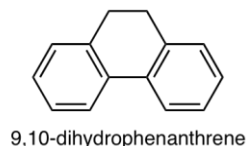
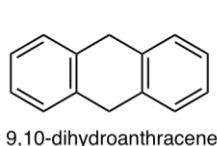
Anthracene:



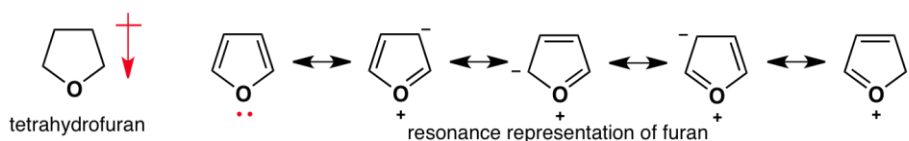
Phenanthrene:



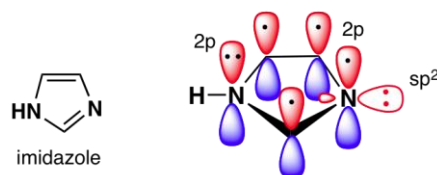
19.2 The 9,10-dihydro product is formed by hydrogenation of the inner ring in both cases; the products still have the aromatic stability of two remaining benzene rings. Any other dihydroproducts have appreciably less aromatic stability.



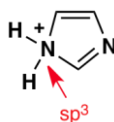
19.3 Due to the high electronegativity of the oxygen atom, the O in tetrahydrofuran is the negative end of the molecular dipole, as indicated below. In furan, one lone pair on oxygen is delocalized into the ring; this transfer of π electron density partially compensates for the inductive effect due to the high electronegativity of O. As a result, the dipole of furan is smaller than that of tetrahydrofuran, but the O is still the negative end.



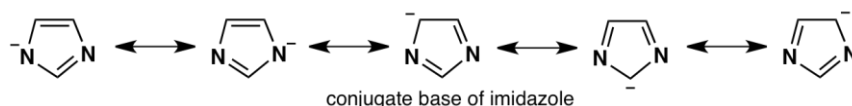
- 19.4** The lone pair on the NH is in a 2p orbital and part of the aromatic system, but the one on the other N is in an sp^2 hybrid orbital orthogonal to the π system.



- 19.5** If protonation occurred at the other N, it would become sp^3 -hybridized and the aromaticity would be lost.

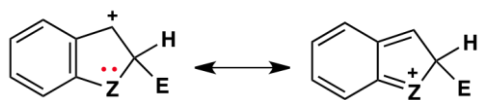


- 19.6** In the conjugate base of imidazole, the negative charge is delocalized as represented below by resonance, and the first two equivalent contributors carrying the formal charge symmetrically on the electronegative nitrogen atoms are the most important. It is the extra stabilization of the conjugate base by the second N (not present in imidazole itself) which accounts for imidazole being more acidic than pyrrole.



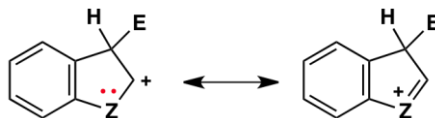
- 19.7** The intermediate formed by attack at C2 has benzylic stabilization but participation of the lone pair of the heteroatom Z involves disruption of the benzenoid ring. In contrast, the intermediate formed by attack at C3 can be stabilized by participation of the lone pair on Z without disruption of the benzene ring, but now there is no benzylic stabilization. In the case of the more electronegative and less polarizable O, benzylic stabilization is dominant, and electrophilic substitution is at C2; in the case of the less electronegative and more polarizable N, heteroatom lone pair participation is dominant, and reaction occurs at C3. It appears that the two stabilizing effects are broadly similar for benzothiophene.

Intermediate following C2 attack:



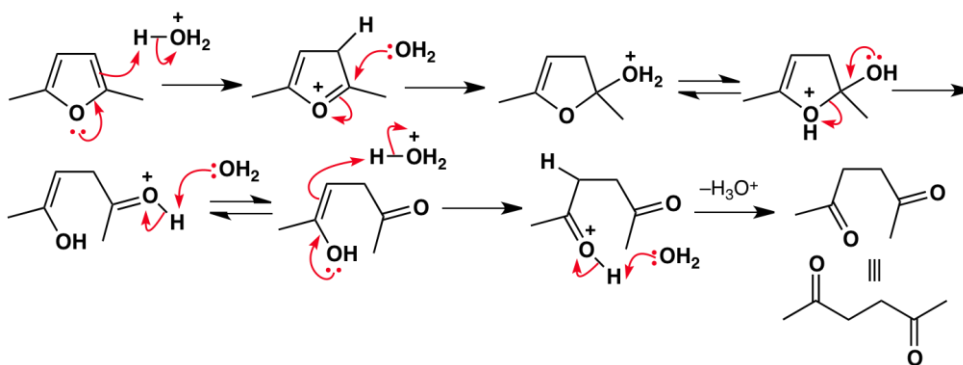
Benzylic stabilization;
participation by Z disrupts benzenoid
ring.

Intermediate following C3 attack:



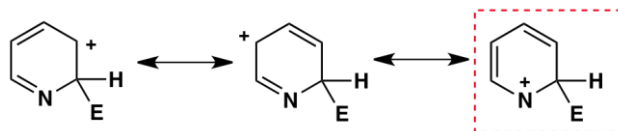
Participation by Z retains benzenoid ring;
no benzylic stabilization.

19.8

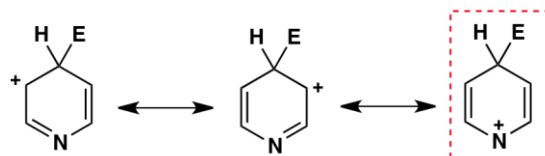


19.9 One of the three resonance contributors to each of the C2 and the C4 intermediates involves the positive charge being on the electronegative N, which makes this contributor less important. In contrast, the C3 intermediate has no such contributor, so this is the most stable and the reaction proceeds mainly *via* this intermediate.

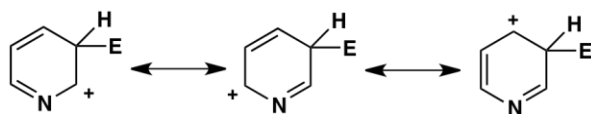
Intermediate in the C2 addition:



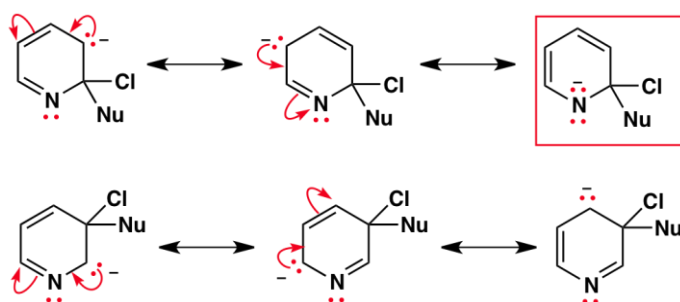
Intermediate in the C4 addition:



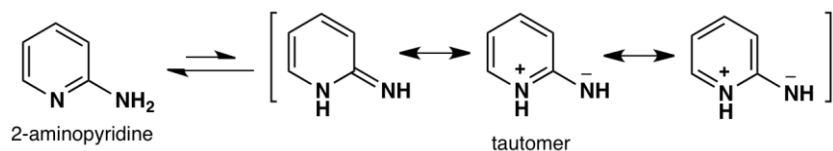
Intermediate in the C3 addition:



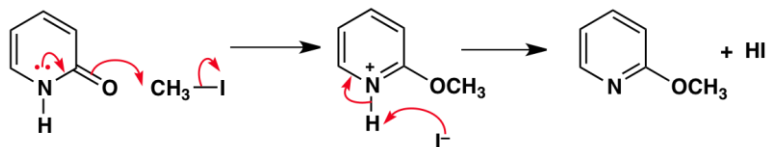
19.10 The carbanion intermediate formed from 2-chloropyridine has a resonance contributor carrying the negative charge on the N, which is favourable. In contrast, all three resonance contributors to the intermediate formed from 3-chloropyridine have the negative charge on less electronegative carbon atoms. Consequently, stabilization of the intermediate following addition of Nu^- in the substitution reaction of 2-chloropyridine is greater than that from 3-chloropyridine, so 2-chloropyridine is the more reactive.



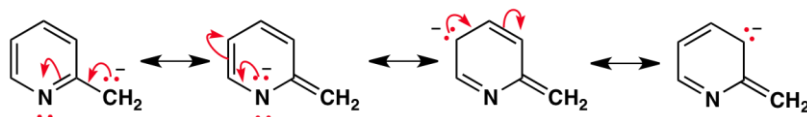
19.11 The two zwitterionic resonance forms of the imine tautomer of 2-aminopyridine which have the cyclic 6 π electron system have the negative charge on the exocyclic N atom. The contribution of these two resonance forms to the overall hybrid of the imine is smaller than the contribution of the analogous two forms of pyridone to its electronic structure because N is appreciably less electronegative than O. So, although pyridone is more stable than 2-hydroxypyridine, 2-aminopyridine is more stable than its imine tautomer.



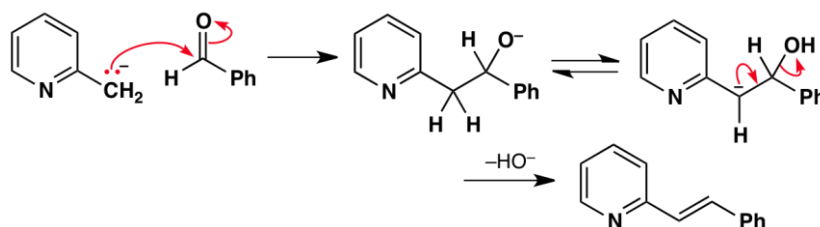
19.12



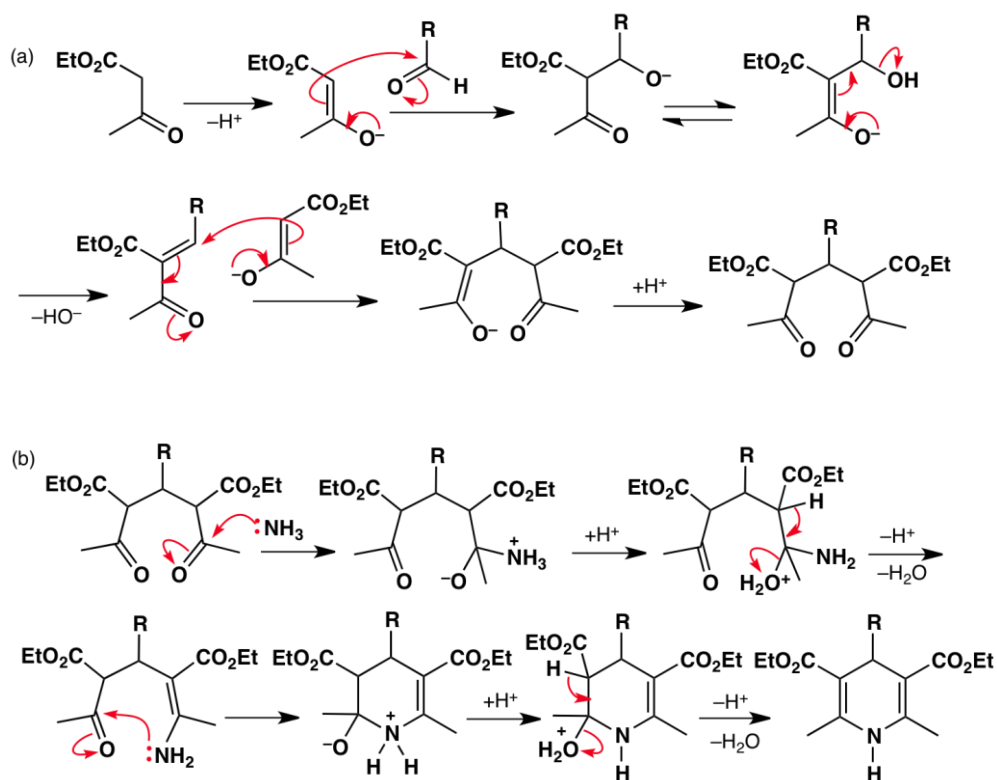
19.13



19.14



19.15



19.16

