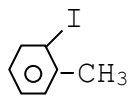
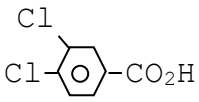
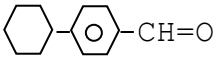
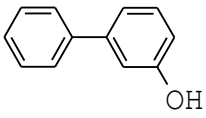
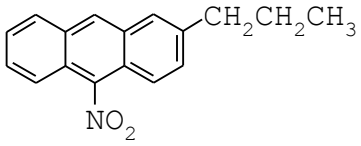
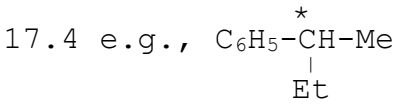
Answers to Puzzles of Chapter 17
Aromatic Compounds and Electrophilic Substitutions

17.1 Countless conjugated π bonds absorb lots of visible light.

17.2 (a) 4-chloro-1-nitrobenzene (b) 2,4-diethylaniline (c) 2-phenyl-1-propanol
(d) 1-bromonaphthalene (e) 4-phenylphenol

17.3 (a)  (b)  (c) 

(d)  (e) 

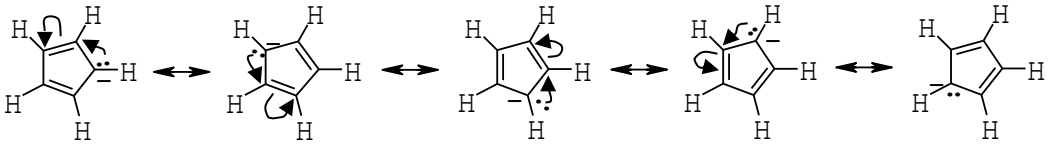
17.4 e.g., 

17.5 (a) Yes: it has a very polar, ionic end. (b) It has both polar and nonpolar sections.
(c) No: it has 18 Cs but only 1 polar, nonionic functional group.

17.6 (a) Energy ↑ 

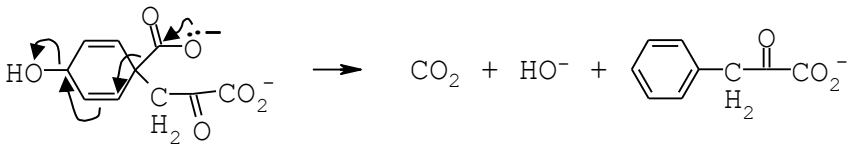
(b) It has both π electrons in a bonding molecular orbital and none in an antibonding orbital.

17.7 Only the 3rd compound is aromatic because it's fully p'd with $6 = 4 \cdot 1 + 2$ π e's.
The 1st has 4 π e's; the 2nd has 4 π e's & is not fully p'd; the 4th is not fully p'd.

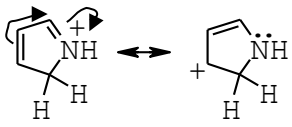
17.8 

17.9 

The 2nd form is aromatic and so a major form. Its charges make the molecule polar.

17.10 (a) 

(b) The 2 - charges on the reactant destabilize it. Also the release of CO_2 gas increases ΔS.

17.11 Resonance only stabilizes the acid protonated at the C: 

17.12 The doubly bonded N: aromaticity does not involve & stabilize its base e's.

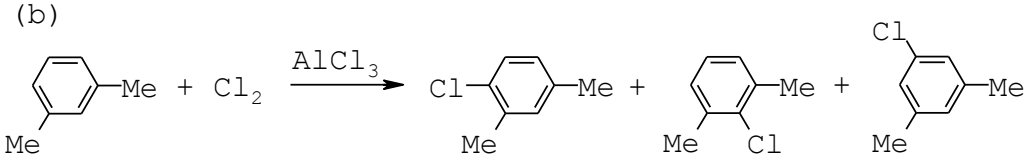
17.13 It's not aromatic: 1 C is sp^3, so its ring is not fully p'd.

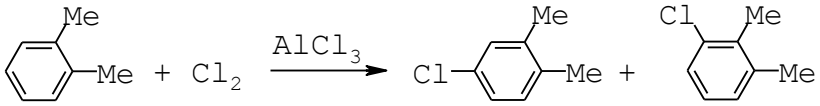
17.14 Not a valid form: its N with 10 e's violates the octet rule.

17.15 $C_6H_6 + HNO_3 \xrightarrow{H_2SO_4} C_6H_5\text{-}NO_2 \xrightarrow{H_2,\ Pt} C_6H_5\text{-}NH_2 \xrightarrow{2\ MeBr} C_6H_5\text{-}NMe_2$

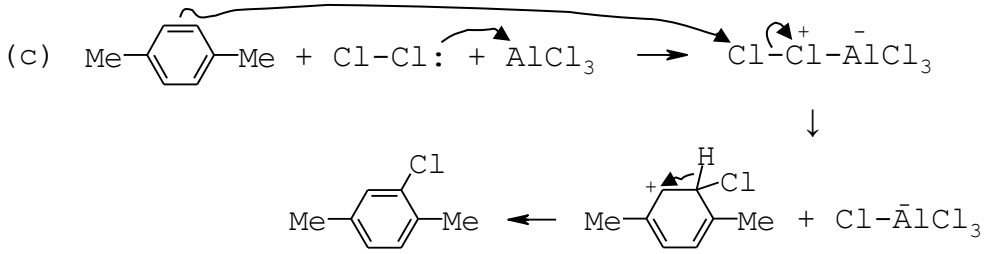
17.16 $C_6H_6 + H_2SO_4 \longrightarrow C_6H_5\text{-}SO_3H \xrightarrow{SOCl_2} C_6H_5\text{-}SO_2Cl \xrightarrow{Et\text{-}OH} C_6H_5\text{-}SO_2O\text{-}Et \xrightarrow{^-C\equiv N} C_6H_5\text{-}SO_3^- + N\equiv C\text{-}Et$

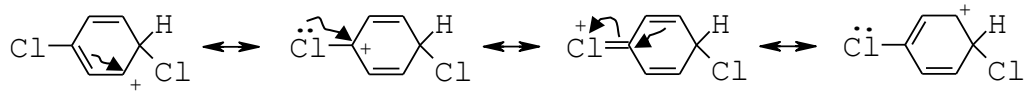
17.17 (a) & (b)

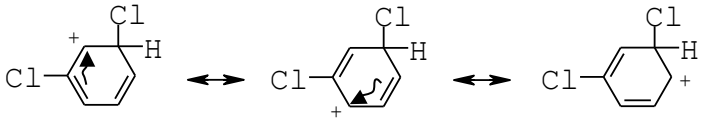
A ≡ 

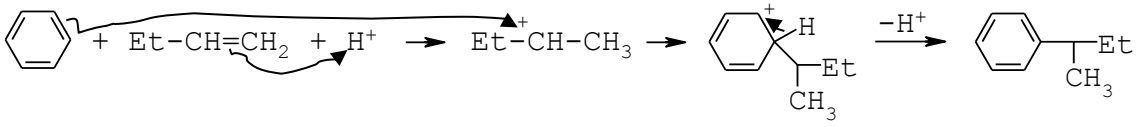
B ≡ 

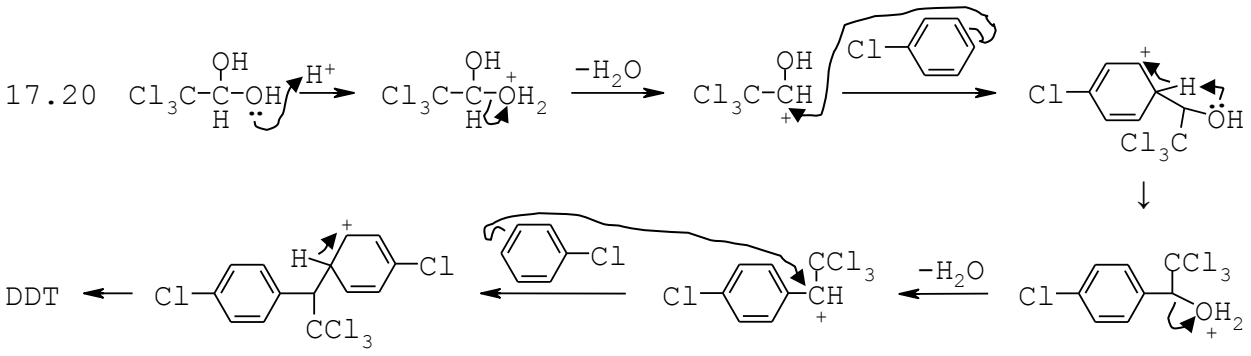
C ≡ 

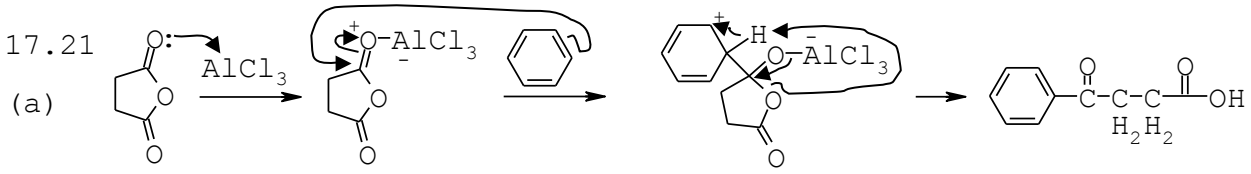
(c) 

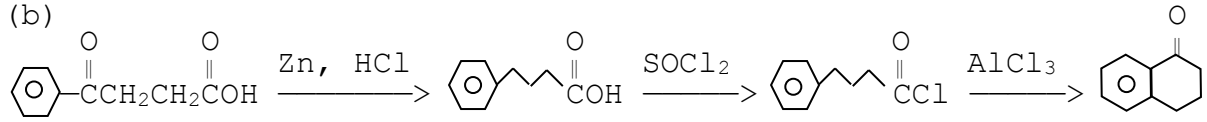
17.18 (a) 

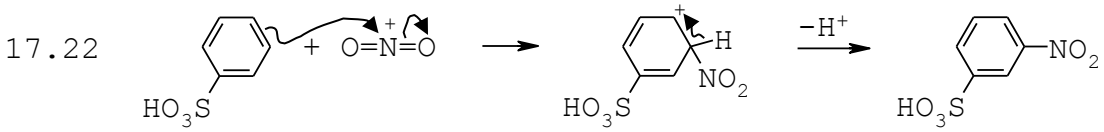
(b) only 3 forms: 

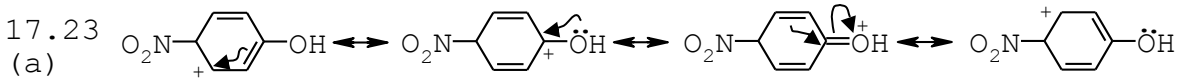
17.19 

17.20 

17.21 (a) 

(b) 

17.22 

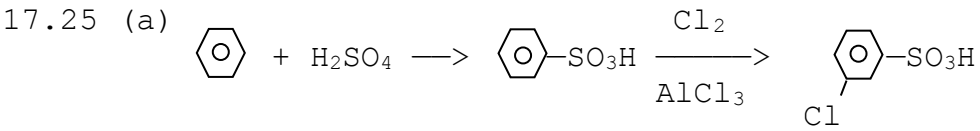
17.23 (a) 

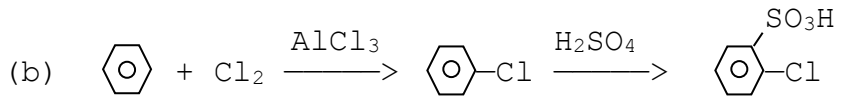
(b) stablest: most bonds

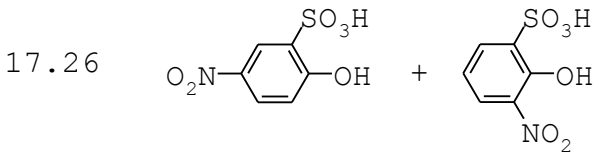
(c) & (d) 

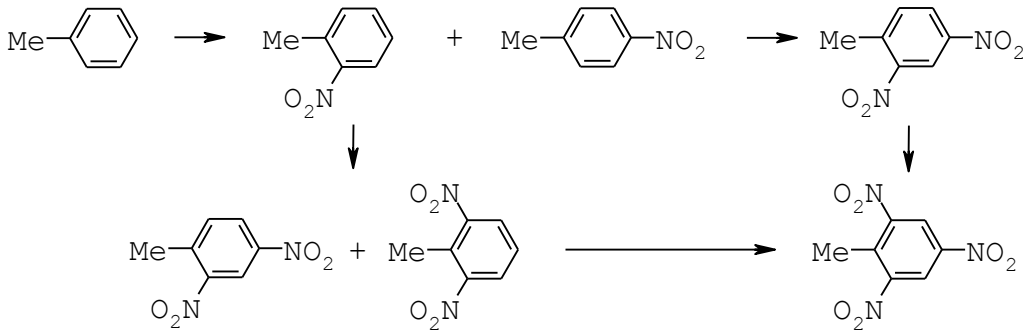
stablest: 3° carbocation

17.24 greater for bromination: $Br\overset{+}{-}Br\overset{-}{-}AlCl_3$ is bigger & more sterically hindered from reacting at the ortho position than $Cl\overset{+}{-}Cl\overset{-}{-}AlCl_3$ is.

17.25 (a) 

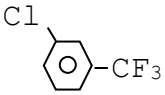
(b) 

17.26 

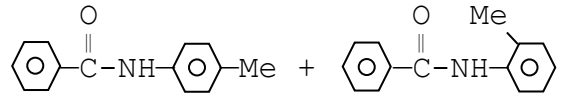
17.27 

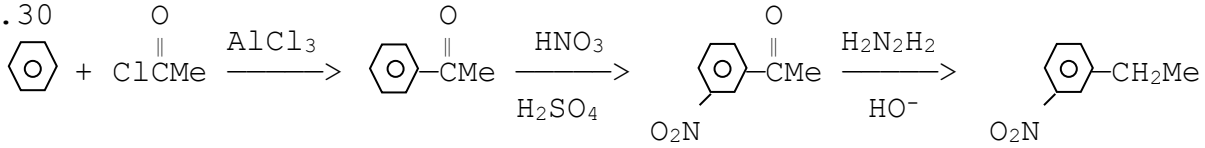
The regioselectivity is consistent with Me being o/p-directing.

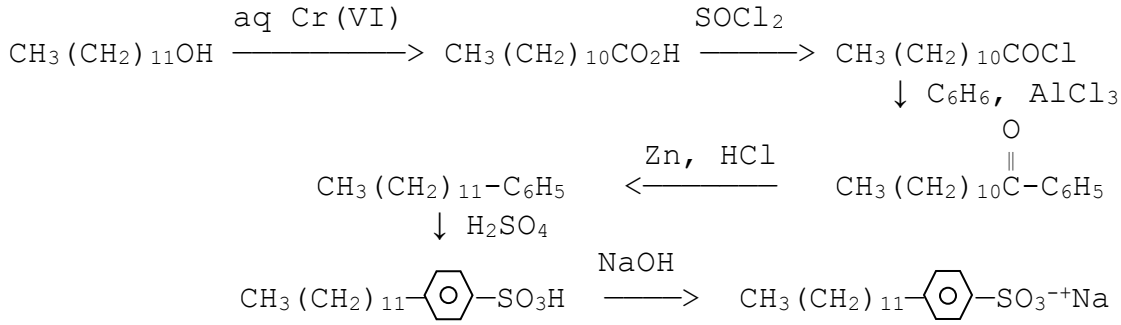
17.28 (a) Benzene: 3 EN F's put a big δ+ on the C by the ring, deactivating the ring.

(b) 

17.29 (a) The phenyl ring on the N: the N's lone pair activates this ring, while the carbonyl's δ+ deactivates the other ring.

(b) 

17.30 

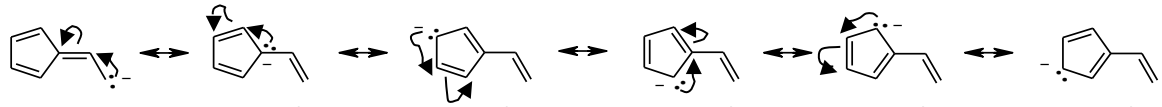
17.31 

17.32 (a) bromobenzene (b) e.g., 1,2-dichlorobenzene (c) 1-chloro-4-ethylbenzene
(d) 2,6-dimethylnaphthalene

17.33 (a) aniline: it is much bigger with more dispersion forces
(b) methylamine: it is more polar with fewer carbons per N

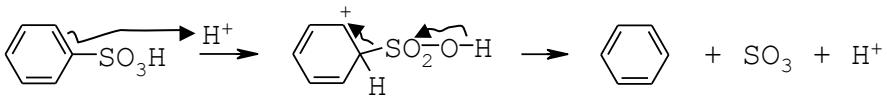
17.34 The 2nd and 3rd compounds because they alone are fully p'd with 4n+2 (i.e., 6) π e's. The 1st has 4 π e's. The 4th is not fully p'd.

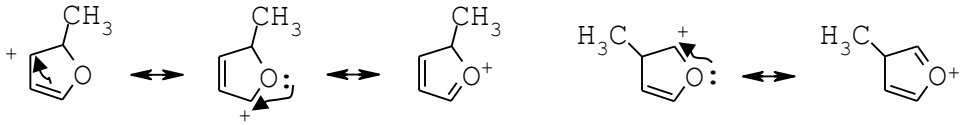
17.35 (a) The conjugate base of the 2nd acid is weaker because aromaticity stabilizes its <u>base e's</u> in most of its resonance forms. So the 2nd acid is stronger.

(b) 

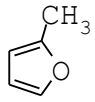
17.36 (a) Only the 1st amine is aromatic because it's fully p'd with 6 π e's.
(b) 2nd amine: no aromaticity stabilizes its base e's; aromaticity stabilizes the 1st amine's base e's.

17.37 (a) H_2SO_4 (b) EtCl, $AlCl_3$ (c) HNO_3, H_2SO_4 (d) Br_2, $AlCl_3$ (e) $ClOCCH_3$, $AlCl_3$
(f) HNO_3, H_2SO_4; then Zn, HCl (g) H_2SO_4; then HO^- (h) $ClOCCH_2CH_3$, $AlCl_3$; then $NaBH_4$
(i) Cl_2, $AlCl_3$; then Mg

17.38 

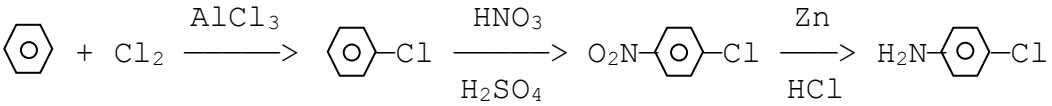
17.39 (a) 

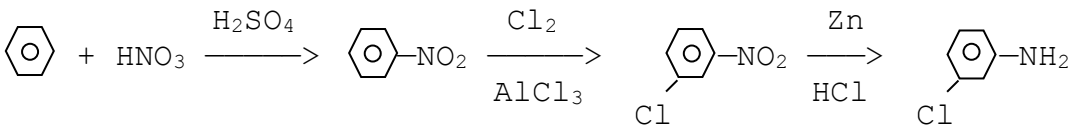
(b) First, because it is more stabilized by more resonance.

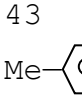
(c) 

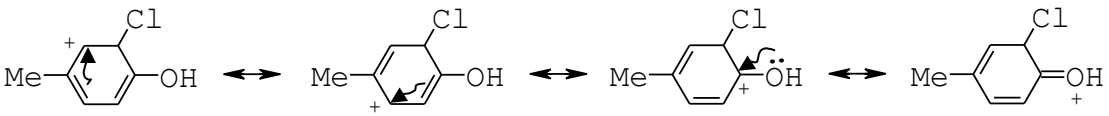
17.40 (a) m (b) o,p (c) m (d) m (e) o,p (f) o,p (g) m (h) o,p (i) m (j) o,p (k) m
(l) o,p (m) m (n) o,p (o) o,p (p) o,p

17.41 In the 4 position the Br is o & p to the o,p-directing Me groups. In the 2 position the Br would be o to the Me groups, but these Me groups would sterically hinder substitution there.

17.42
(a) 

(b) 

17.43 
Me, OH because more resonance stabilizes its intermediate:

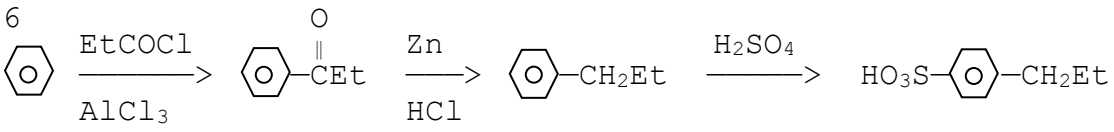


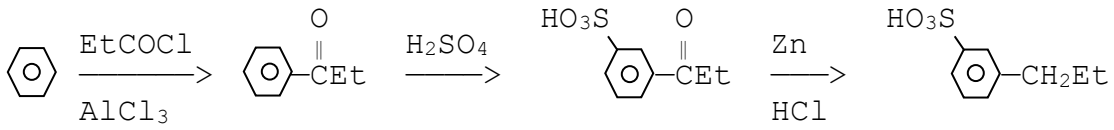
17.44 The NH_2 group in acid becomes $^+NH_3$, which is meta directing and deactivating.

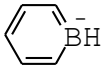
17.45 (a) deactivating (b) activating (c) deactivating (d) deactivating (e) activating

(f) activating (g) deactivating (h) activating (i) deactivating (j) activating (k) deactivating (l) deactivating (m) deactivating (n) activating (o) activating (p) activating

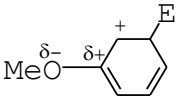
17.46

(a) 

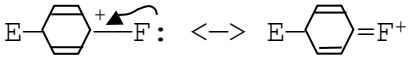
(b) 

17.47 (a)  (b) Aromatic because it's fully p'd with 6 π e's.

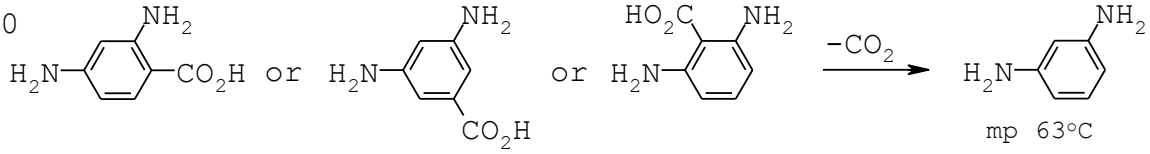
17.48 The δ+ from the EN O destabilizes the intermediate +, & resonance with Ö can't occur:



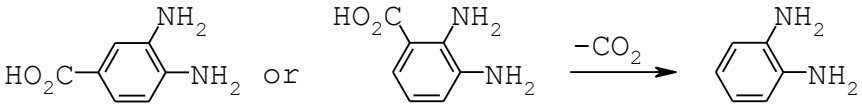
17.49 Unlike the other halogens F is about the same size as C. So it greatly stabilizes the cation intermediate of ortho or para substitution with a fourth, stablest resonance form:



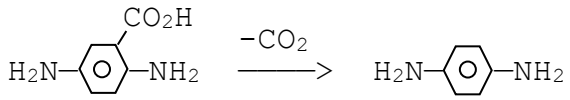
17.50

(a) 

mp 63°C

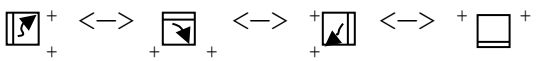


mp 104°C

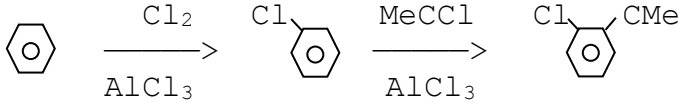


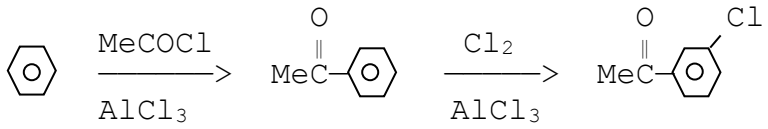
mp 142°C

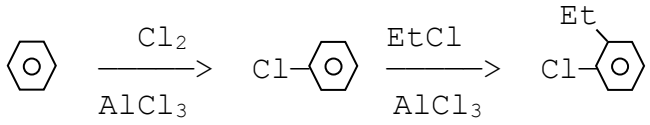
(b) With 3 symmetry planes it is the most symmetric.

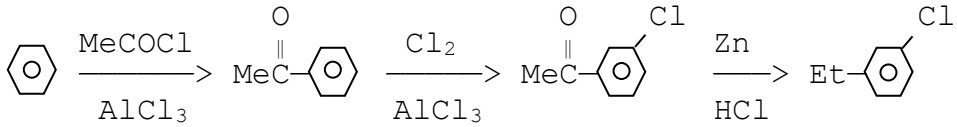
17.51 (a) & (b) 

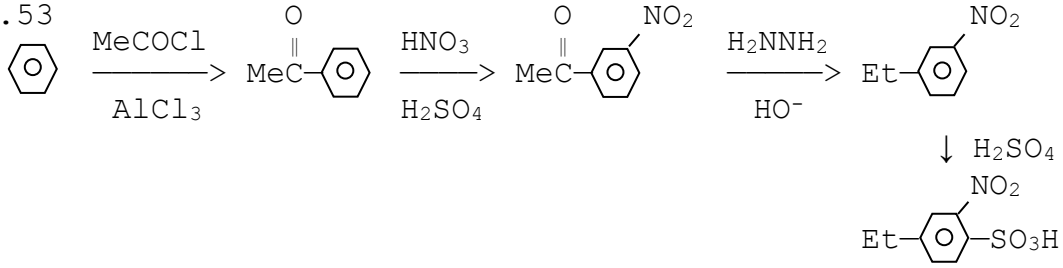
17.52

(a) 

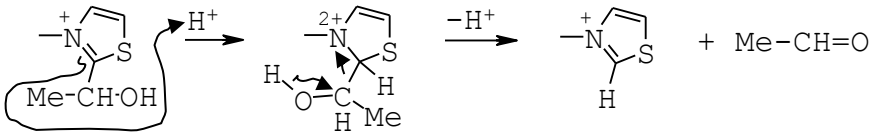
(b) 

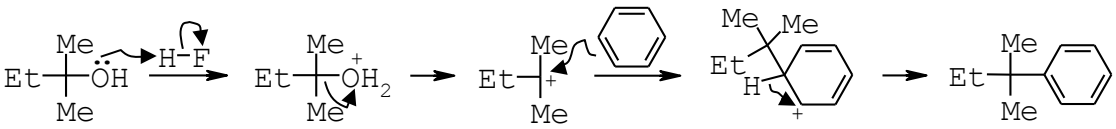
(c) 

(d) 

17.53 

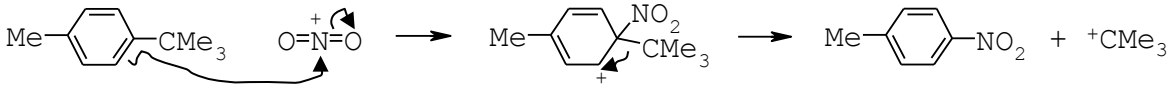
17.54 (a) Both rings are aromatic: fully p'd with 6 π e's.

(b) 

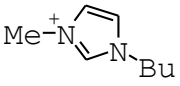
17.55 

17.56 Only 2 repelling e⁻ pairs (in 2 σ bonds) repel pyridine's base e's, while 3 repelling e⁻ pairs (in 3 σ bonds) repel methylamine's base e's.

17.58 (a) Steric hindrance by the large CMe_3 group limits substitution at the C ortho to it.

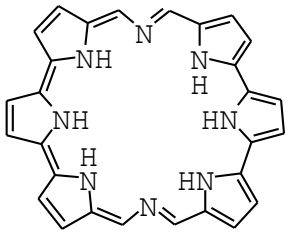
(b) 

17.59 Hydrogenation is reversible. So Pd catalyzes dehydrogenation as well as hydrogenation.

17.60 (a) Aromatic: fully p'd with 6 π e's. (b) 

17.61 Aromatic: fully p'd with 6 π e's (lone pairs on N's).

17.62 These 15 conjugated π bonds compose an aromatic ring:



1/11