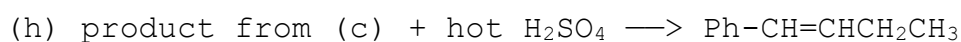
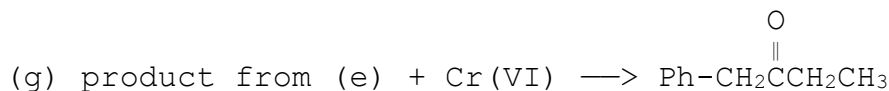
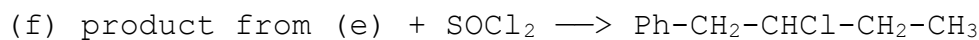
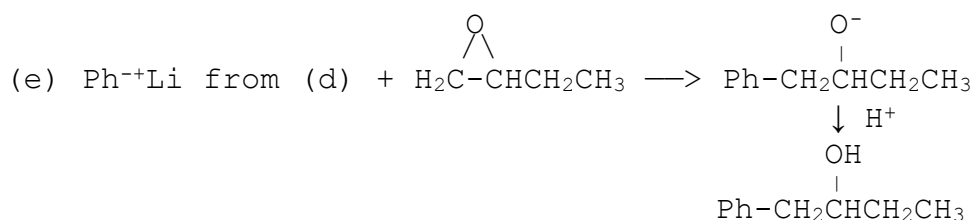
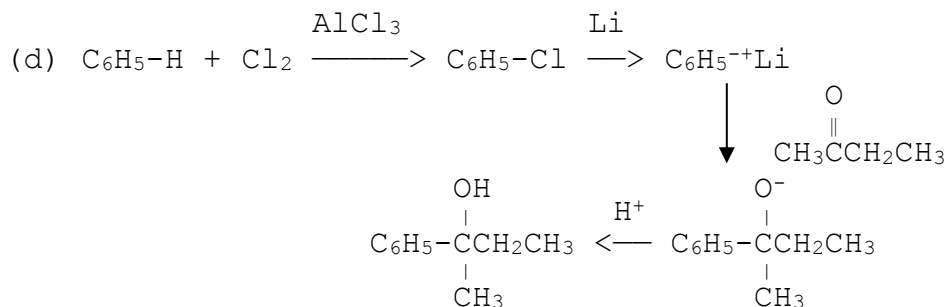
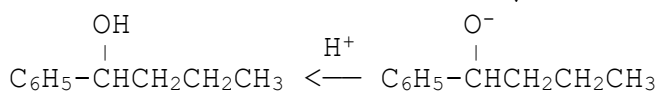
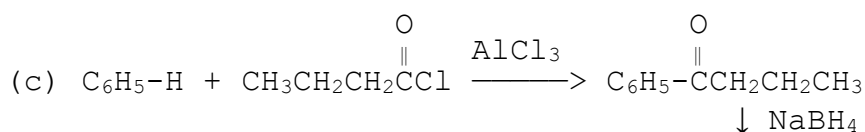
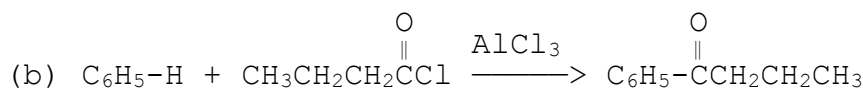
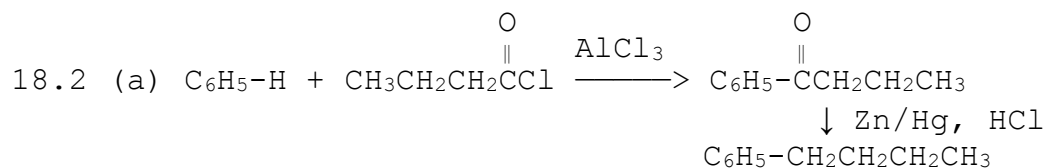
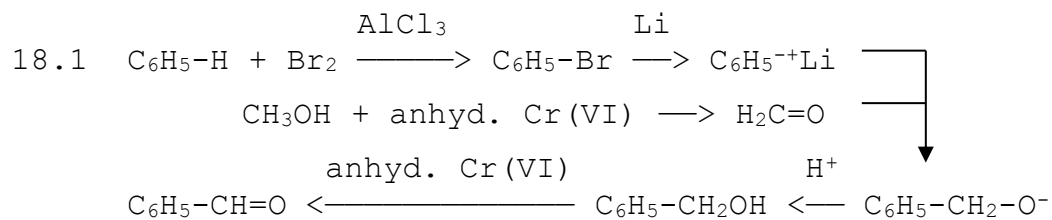
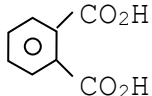
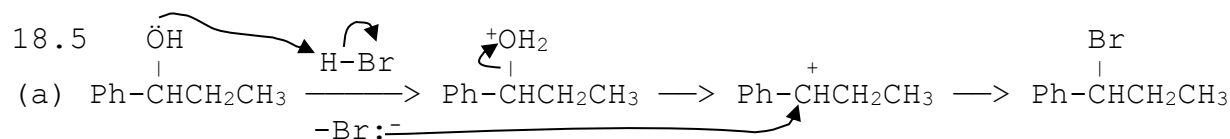


Answers to Puzzles of Chapter 18  
Further Chemistry of Benzene Compounds



(d)  $C_6H_5-CO_2H$  (e) no reaction (f) 

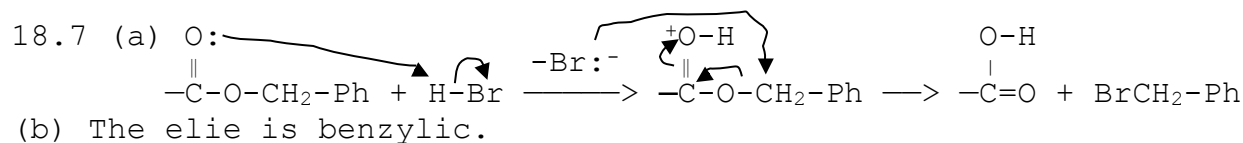
18.4 No because the electrophile is  $1^\circ$  and not benzylic.



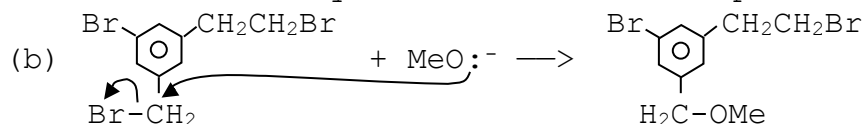
(b) It is unlikely because the resonance stabilization of a benzylic  $C^+$  would be lost.

(c) This reaction because in the rls (the second step) a stabler benzylic  $C^+$  forms.

18.6 (a)  $PhCH_2NH_2$  (b)  $PhCH_2CH_3$  (c)  $PhCH_2CH_2NH_2$  (d) a mess

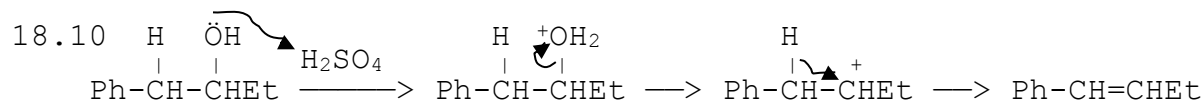


18.8 (a) The benzylic Br because this position promotes  $S_N2$ .



(c) The phenyl Br because the phenyl position hinders  $S_N2$

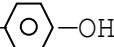
18.9  $Ph-OH + ICH_2CH_3$  (no further reaction)



18.11 (a)  $PhCH=CHCH_3$  (b)  $CH_2=CHCH=CHCH_3$  (c)  $PhCH=CHCH_2CH_3$   
 (d)  $CH_2=CHCH=CHCH_2CH_3$  (e)  $PhCH_2CH=CHCH_2CH_3 + PhCH_2CH_2CH=CHCH_3$   
 (f)  $CH_2=CHCH_2CH=CHCH_2CH_3 + CH_2=CHCH_2CH_2CH=CHCH_3$  (g)  $PhCH_2CH=CHCH_3$   
 (h)  $CH_2=CHCH_2CH=CHCH_3$

18.12 Aromaticity stabilizes the  $\pi$  bonds of the ring.

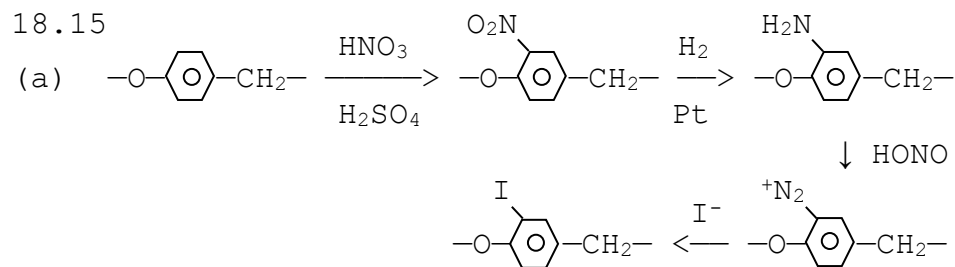
18.13 (a)  $Ph-CHI-CH_3$  (b)  $Ph-CHI-CH_2CH_3$

(c)  $Ph-CH_2-CHI-CH_3 + Ph-CHI-CH_2-CH_3$  (d)  $Ph-CH_2-CHI-$  $-OH$  only

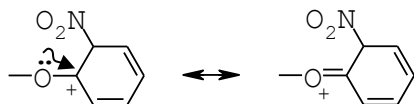
(e)  $Ph-CH=CH-CHI-CH_3 + Ph-CHI-CH=CH-CH_3$  (f)  $Ph-CHI-CHOH-CH_3$

18.14 (a) The C would be *sp* hybridized and linear.

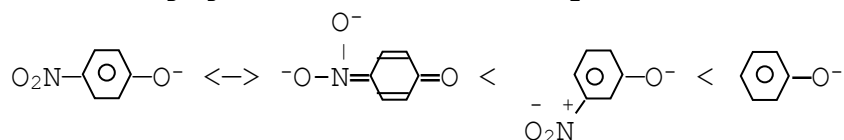
(b) No: the empty *p* orbital would be in the plane of the ring, not parallel with the other *p* orbitals.



(b) Because extra resonance with the ortho O can stabilize the intermediate:

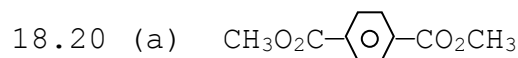
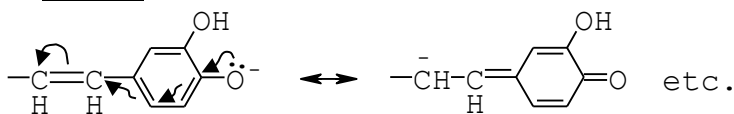


18.16 conjugate bases' basicity:



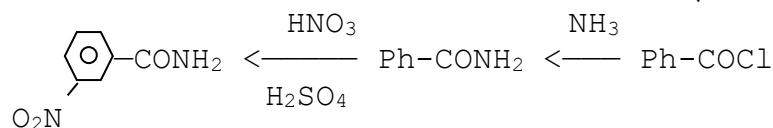
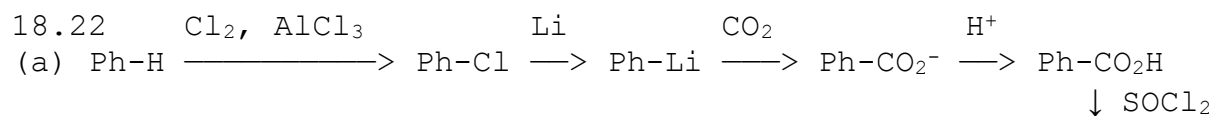
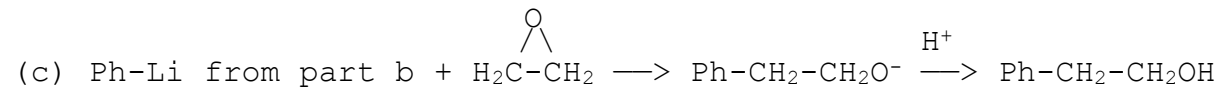
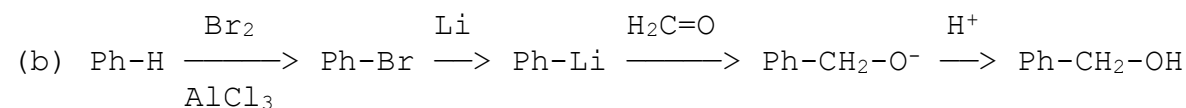
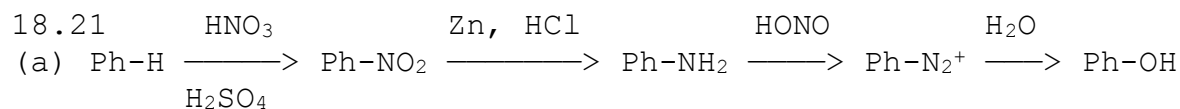
The extra resonance form in the 1st base stabilizes its base e's the most. The + on the nitro group of the 2nd base inductively stabilizes its base e's.

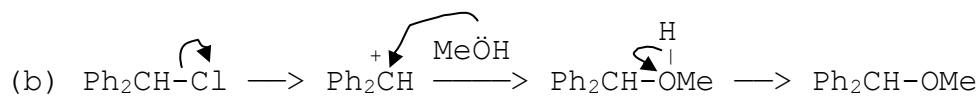
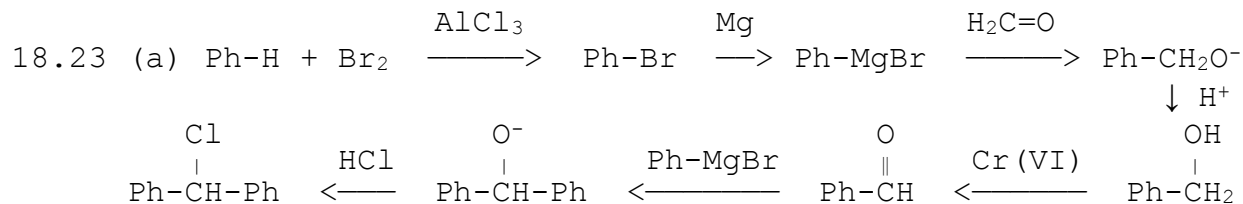
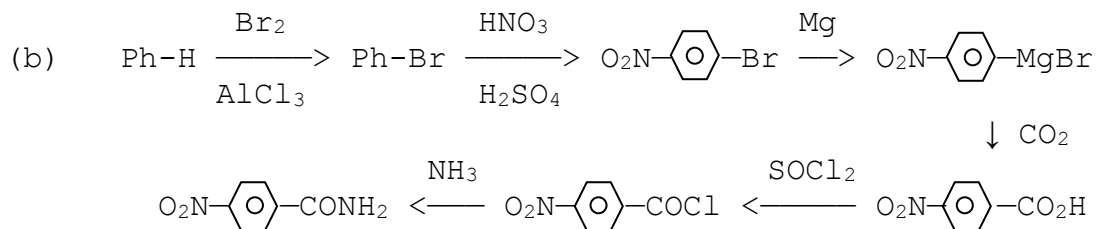
18.17 (a) The carboxylic acid H is most acidic. (b) No: alcohols are less acidic than phenols. (c) The hydroxy group para to the alkenyl group: more resonance forms stabilize its conjugate base's base e's more:



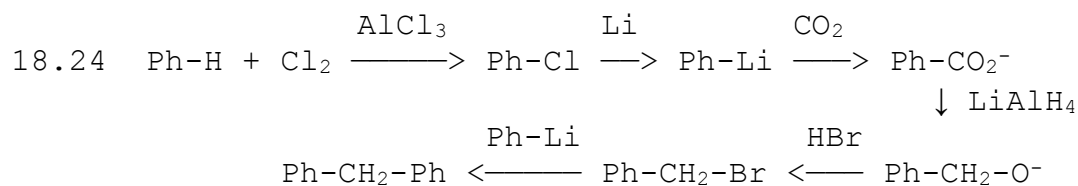
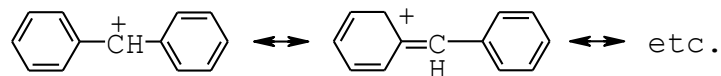
(b) IR: 3010  $\text{cm}^{-1}$  (w):  $sp^2$  C-H; 3000-2900  $\text{cm}^{-1}$  (s):  $sp^3$  C-H; 1720  $\text{cm}^{-1}$  (s): conj. C=O; 1115  $\text{cm}^{-1}$  (s): C-O; 730  $\text{cm}^{-1}$  (s):  $sp^2$  C-H

NMR:  $\delta$  8.1 (s): Ar H;  $\delta$  3.9 (s):  $\text{CH}_3$

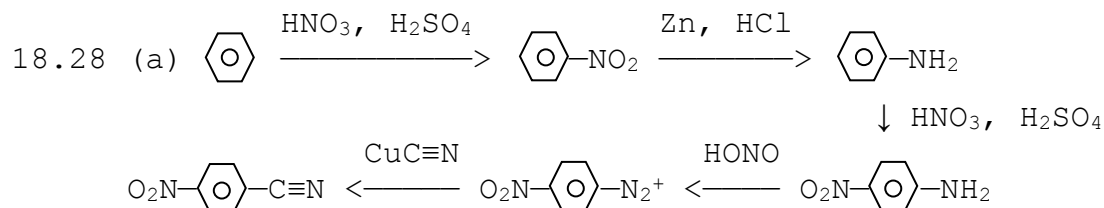
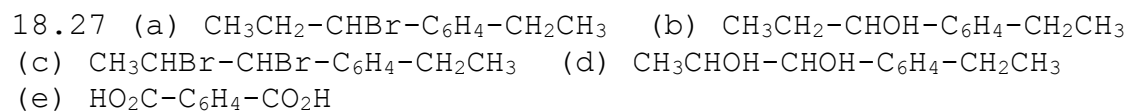
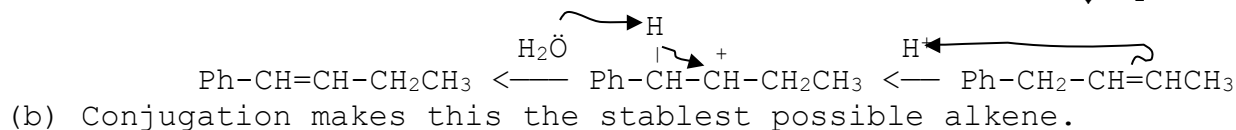
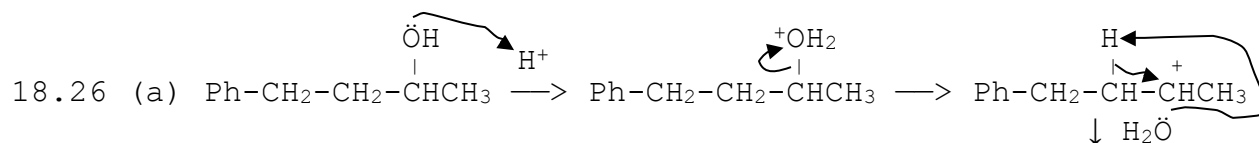
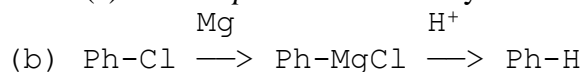


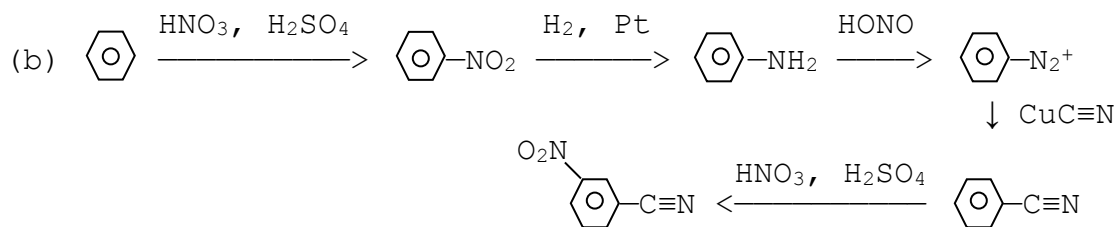


(c) Faster: more benzylic resonance stabilizes the C<sup>+</sup> more:



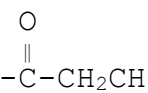
18.25 (a) No: an *sp*<sup>2</sup> carbon normally does not undergo nucleophilic substitution.



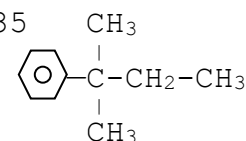


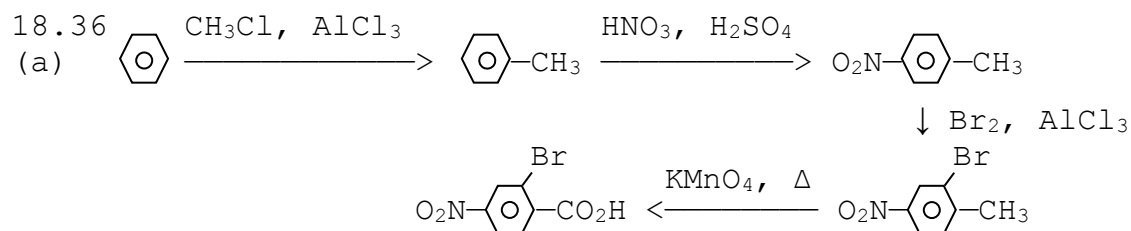
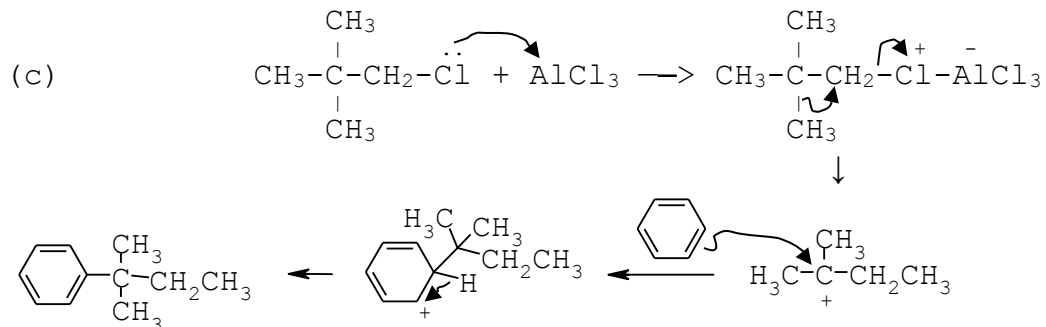
18.29 (a)  $\text{Ph-O}^- + \text{H}_2\text{O}$  (b)  $K = K_a \text{ of PhOH} / K_a \text{ of H}_2\text{O} = 1 \times 10^{-10} / (2 \times 10^{-16}) = 10^6$   
 (c) Products predominate because  $K > 1$ .

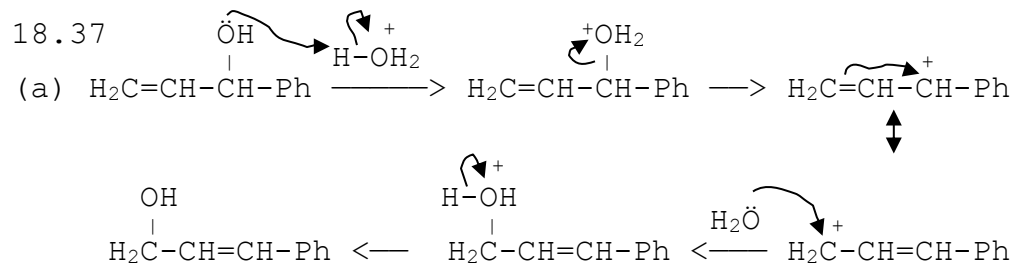
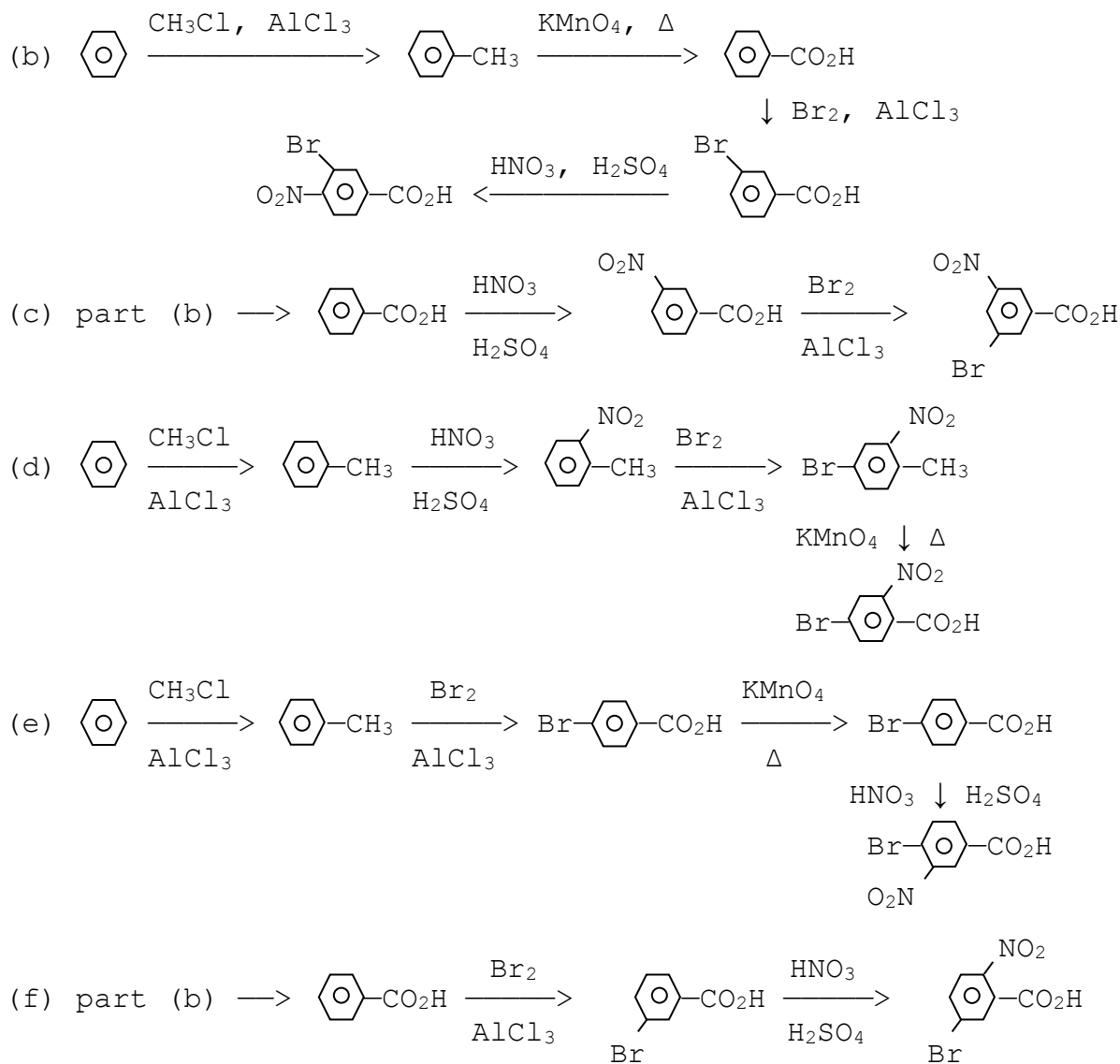
18.30 (a)  $\text{Me-O}^- + \text{H}_2\text{O}$  (b)  $K = K_a \text{ of MeOH} / K_a \text{ of H}_2\text{O} = 3 \times 10^{-16} / (2 \times 10^{-16}) = 1.5$   
 (c) Products very slightly predominate because  $K > 1$ .

18.33 (a)   
 (b) IR: 3100-3000  $\text{cm}^{-1}$ :  $sp^2$  C-H; 3000-2900  $\text{cm}^{-1}$ :  $sp^3$  C-H; 1680  $\text{cm}^{-1}$ : conj. C=O;  
 1600  $\text{cm}^{-1}$ : phenyl C=C; 950, 740, 690  $\text{cm}^{-1}$ :  $sp^2$  C-H bend  
 $^1\text{H NMR}$ :  $\delta$  8.0-7.4: Ar-H; 3.0 (q):  $\text{CH}_2$ ; 1.2 (t):  $\text{CH}_3$

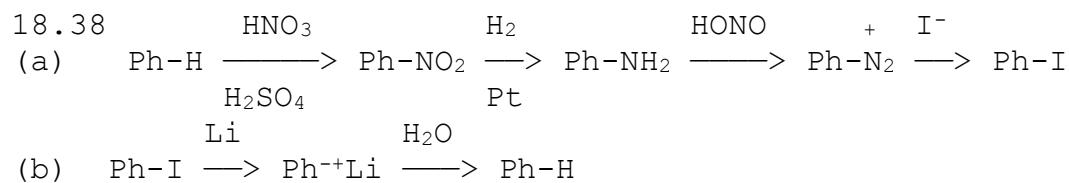
18.34 No: this would require  $\text{S}_{\text{N}}1$  or  $\text{S}_{\text{N}}2$  on an  $sp^2$  C of a benzene ring, which is very difficult.

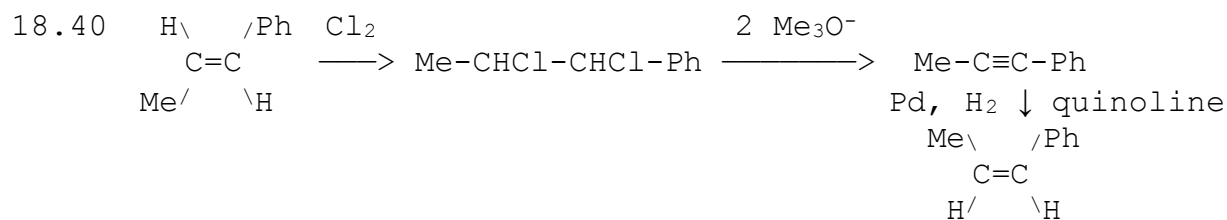
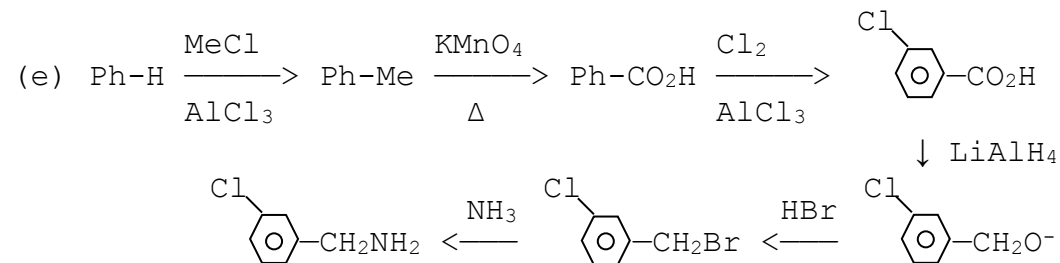
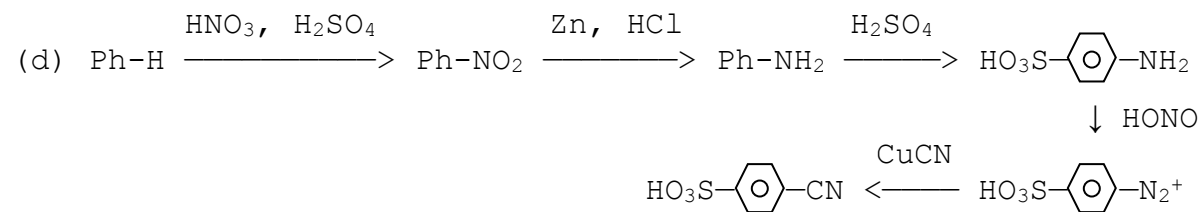
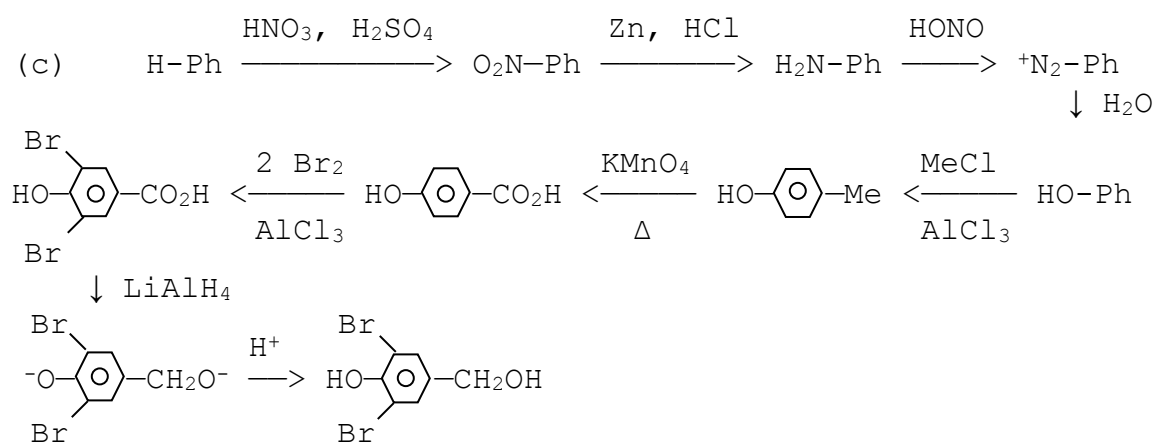
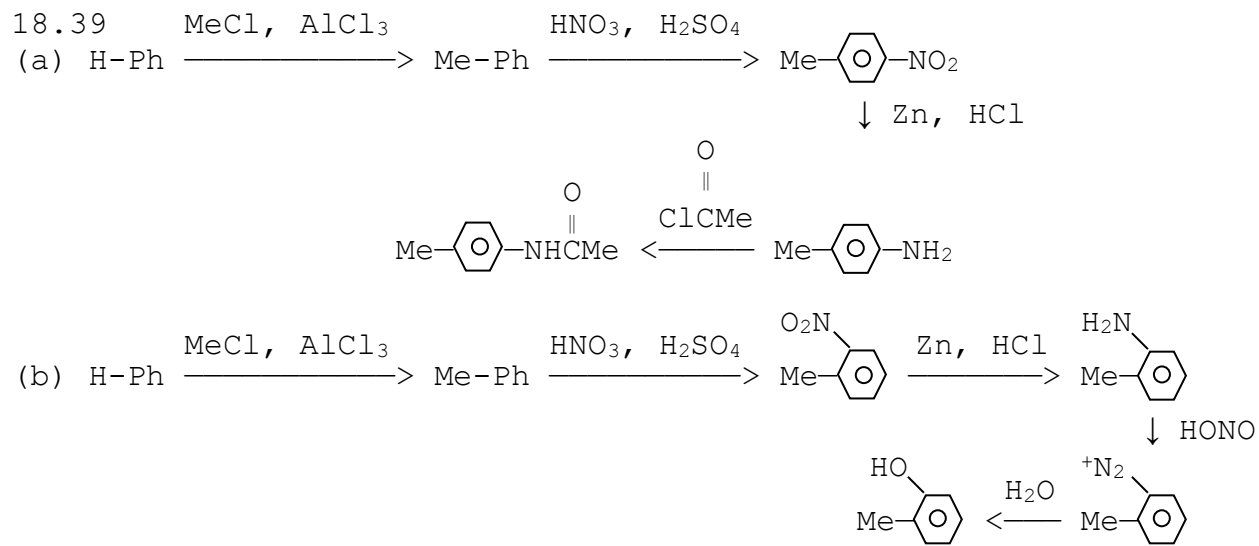
18.35 (a)   
 (b)  $\delta$  7.1: Ar-H;  $\delta$  1.6:  $\text{CH}_2$ ;  $\delta$  1.2: Ar-C-( $\text{CH}_3$ )<sub>2</sub>;  $\delta$  0.9:  $\text{CH}_2\text{CH}_3$



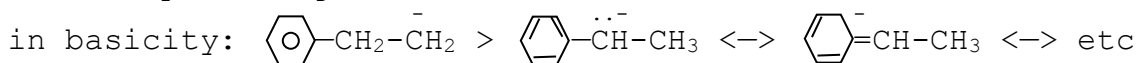


(b) The second alcohol predominates because the equilibrium between the two isomers favors the stabler alkene, conjugated with the benzene ring.





18.41 Compare conj. bases:



because resonance stabilizes the base e's of the second base. So  $\text{Ph-CH}_2\text{-CH}_3$  are more acidic.

