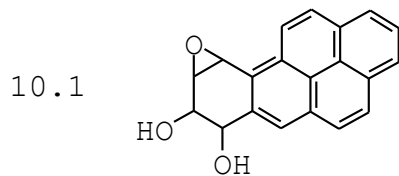
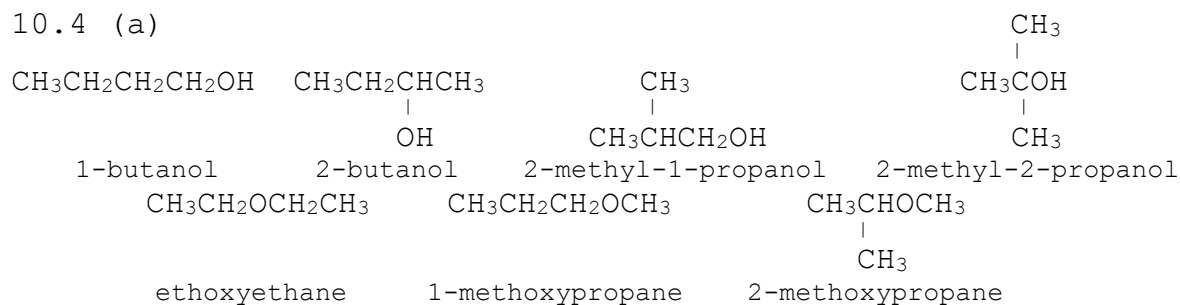
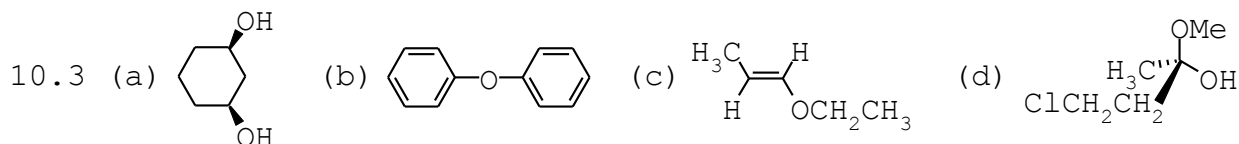


Answers to Puzzles of Chapter 10
Alcohols and Ethers



10.2 (a) 1-methoxy-2-methylbutane (b) 4-ethoxy-1-pentanol
(c) 1-bromo-2,2-dimethoxypropane (d) 1-phenoxy-2-propoxycyclopentane



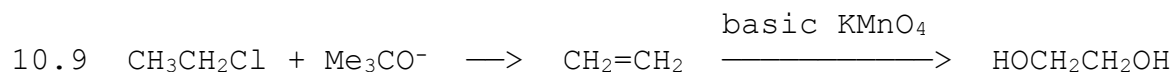
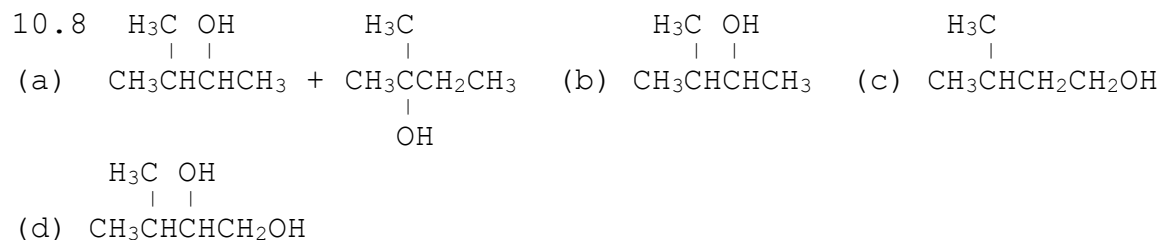
(b) 1-butanol has the highest bp because it has hydrogen "bonds" and the largest surface area.
(c) With 1 chiral atom 2-butanol has two enantiomer stereoisomers

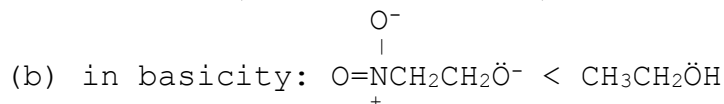
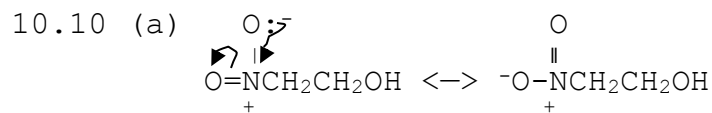
10.5 (a) 1,2-ethanediol, because it has more H "bonds"
(b) 1,2-ethanediol, because it has more surface area (c) water, more volatile

10.6 (a) in H_2O -solubility: 2-methyl-1-butanol > 1-pentanol > 3-methyl-1-pentanol
because 2-methyl-1-butanol has the most compact nonpolar part, and 3-methyl-1-pentanol has the largest nonpolar part.

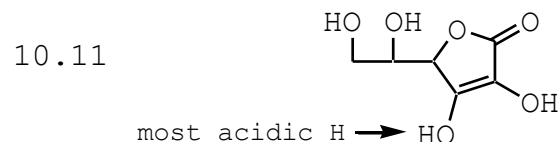
(b) in bp: 2-methyl-1-butanol < 1-pentanol < 3-methyl-1-pentanol
because increasing surface area increases dispersion forces.

10.7 Not soluble because cholesterol is only very slightly polar

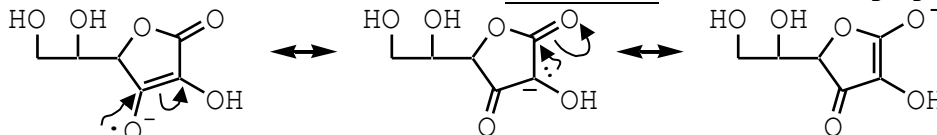




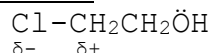
because the + attracts & stabilizes the base e's. So 2-nitro-1-ethanol is the stronger acid.



Resonance most stabilizes the base e's of its conjugate base:

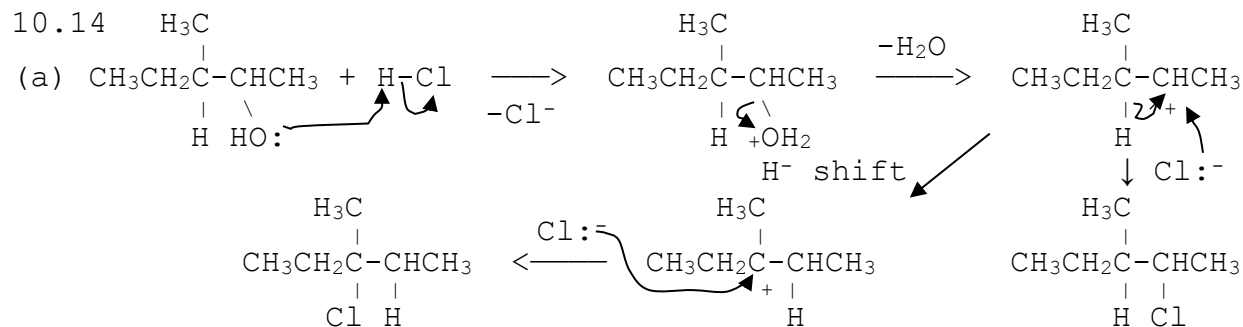


10.12 (a) 2-chloro-1-ethanol is the weaker base because the χ Cl puts a δ^+ on the C, which attracts & stabilizes the base e's inductively:

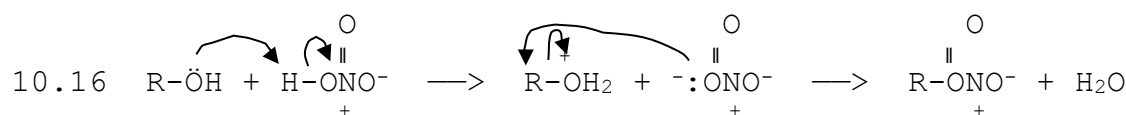
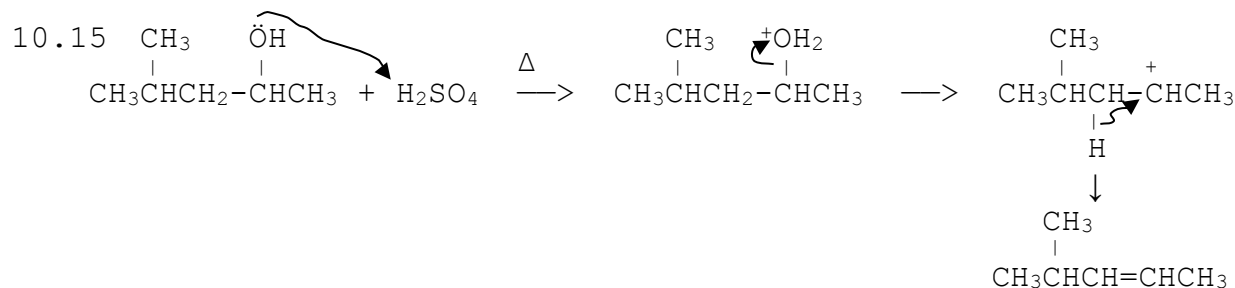


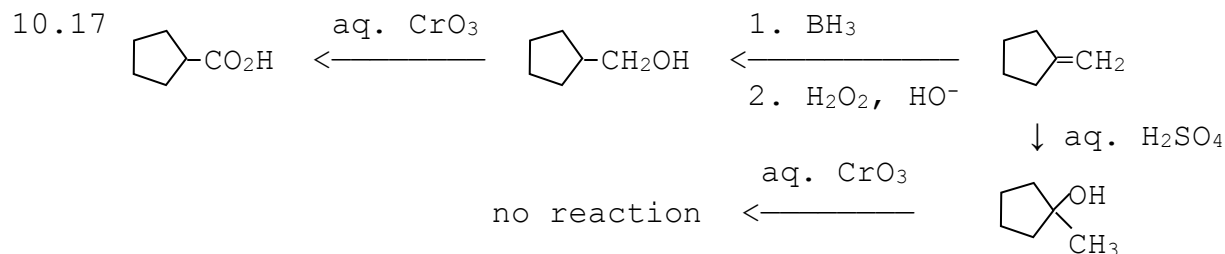
(b) They would permit equally fast E1 reactions because the base does not react in the rls.

10.13 (a) $\text{Me}_3\text{CBr} + \text{Me}_3\text{COH}$ by $\text{S}_{\text{N}}1$ (b) $\text{Me}_2\text{C}=\text{CH}_2$ by E1



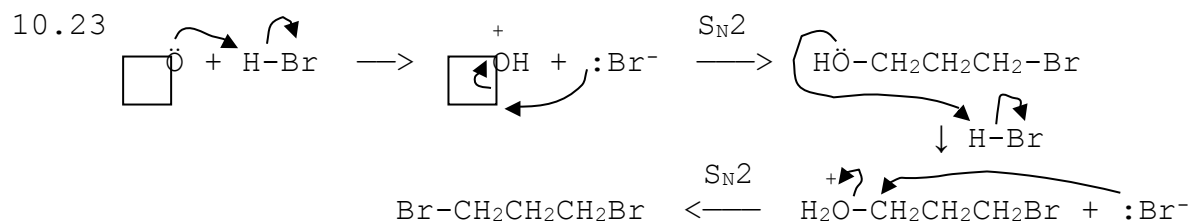
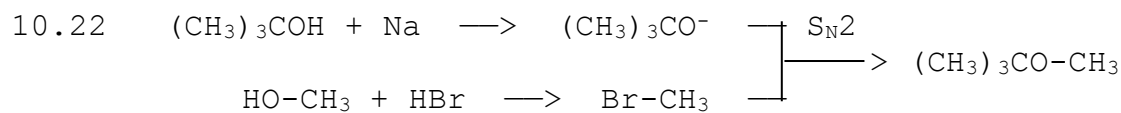
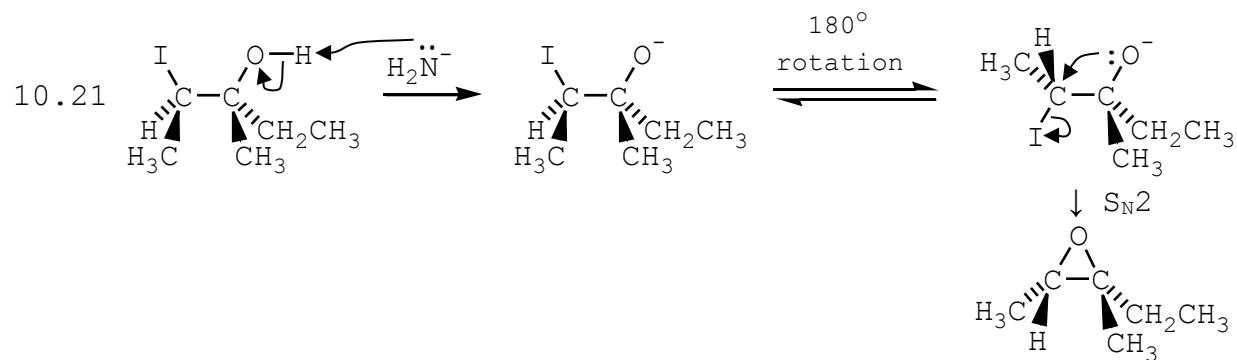
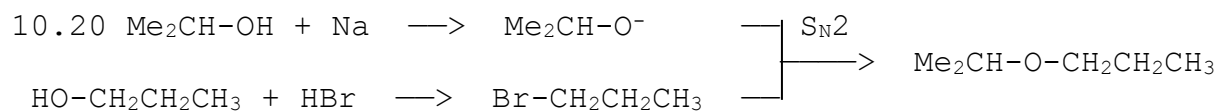
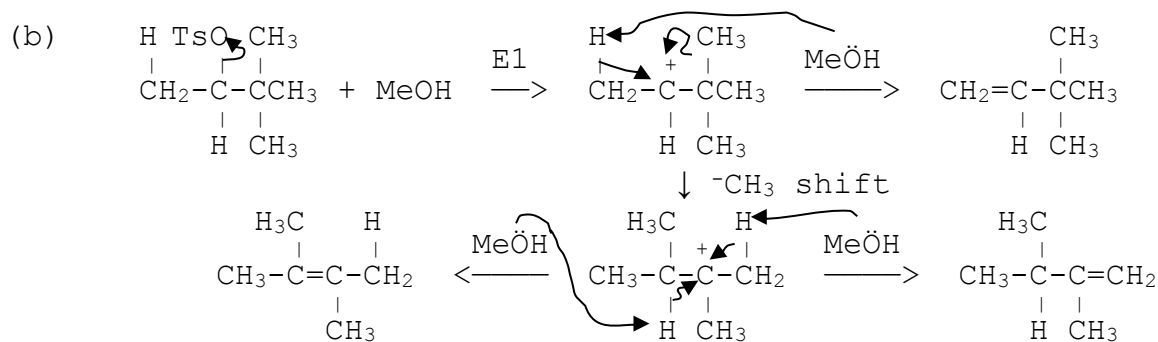
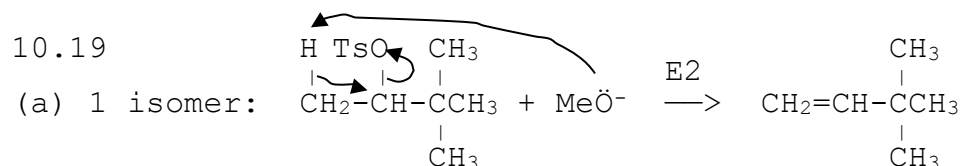
(b) With SOCl_2 no C^+ rearrangement occurs, so 2-chloro-3-methylpentane predominates.

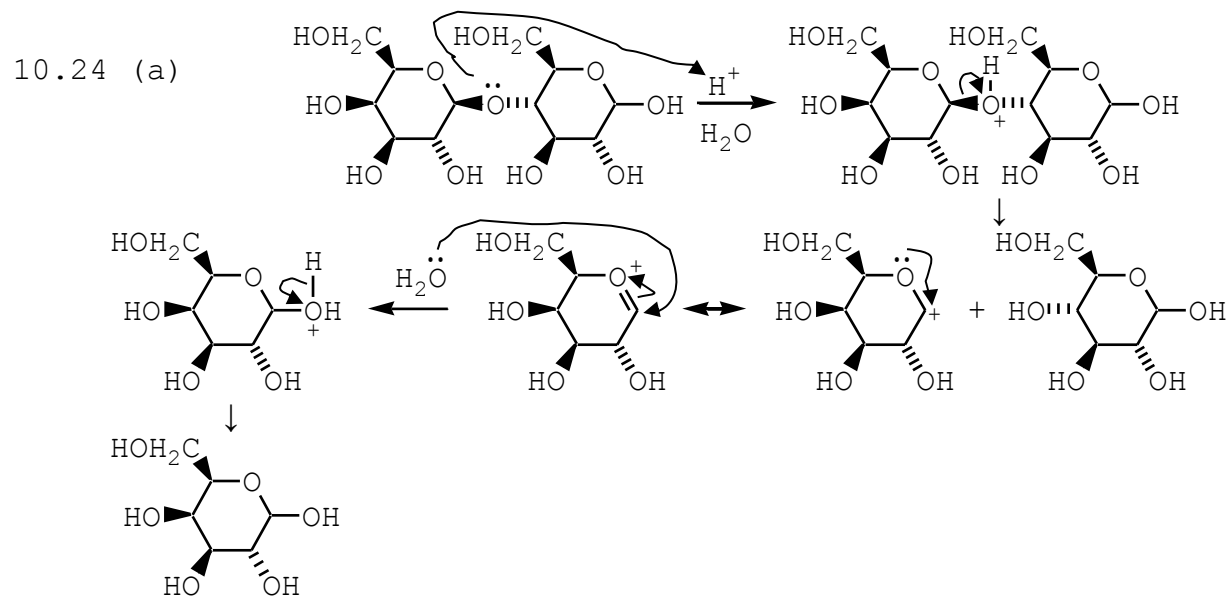




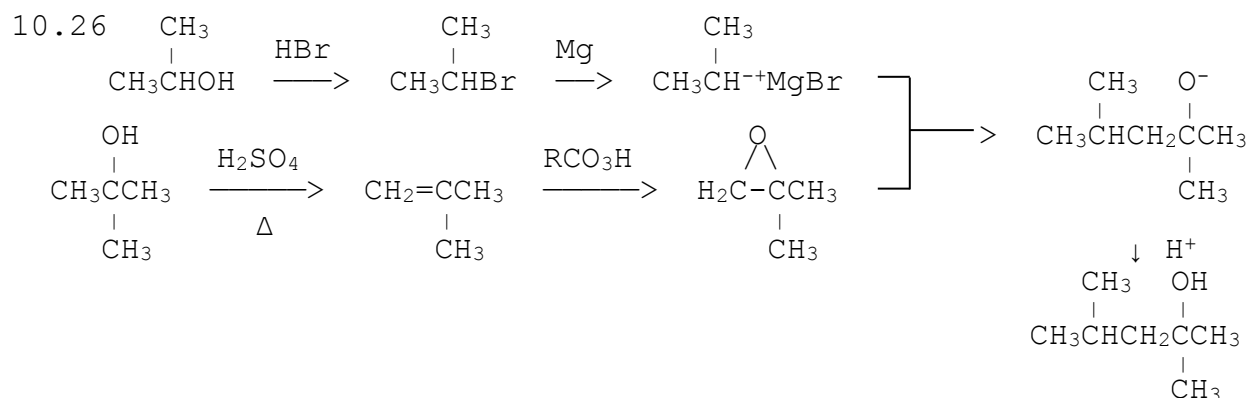
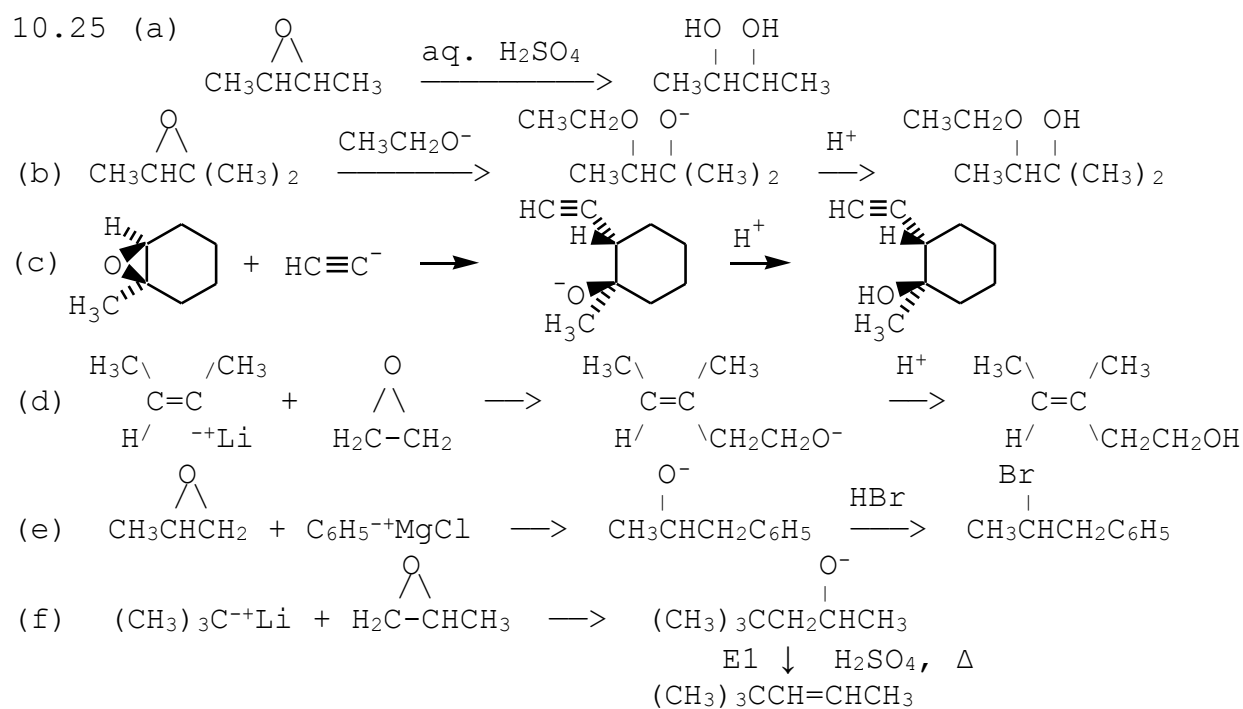
10.18 (a) Ethanol decreases the blue light absorbed because it reduces $\text{Cr}_2\text{O}_7^{2-}$.

(b) ethanoic (acetic) acid (c) no, because it can't be oxidized by Cr(VI)





(b) Only the carbocation stabilized by resonance forms.



10.27 (a) 4-iodo-2-butanol (b) (*R*)-1-methoxy-1-propanol (c) (*Z*)-2-chloro-2-butene-1,4-diol
 (d) *trans*-1-ethoxy-3-propoxycyclobutane

10.28 (a) 1-bromo-1-ethoxyethene: $\text{CH}_2=\text{CBr}-\text{OCH}_2\text{CH}_3$

(b) 1-methoxybutane: $\text{CH}_3\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$

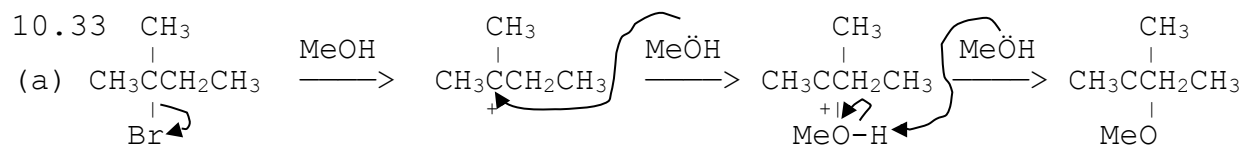
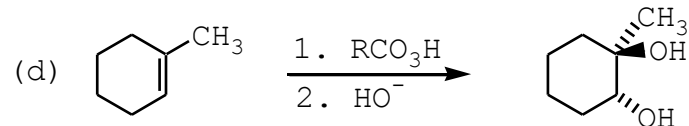
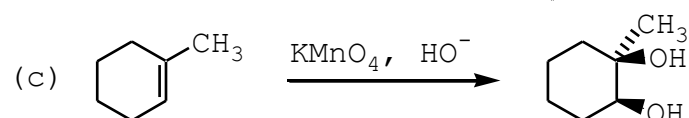
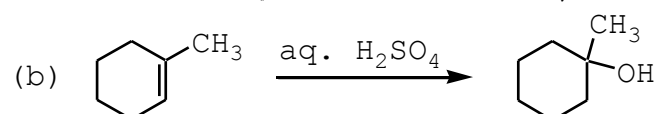
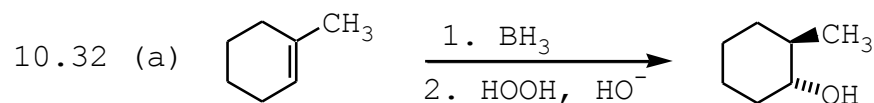
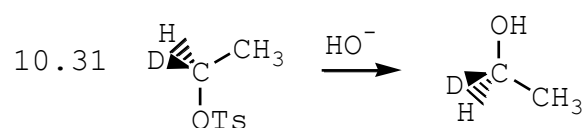
(c) 5-chloro-2-pentanol: $\text{CH}_3-\text{CHOH}-\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$

(d) e.g., 2,2-dimethoxypropane: $(\text{CH}_3)_2\text{C}(\text{OCH}_3)_2$

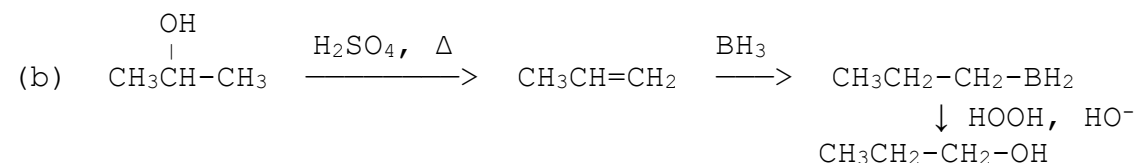
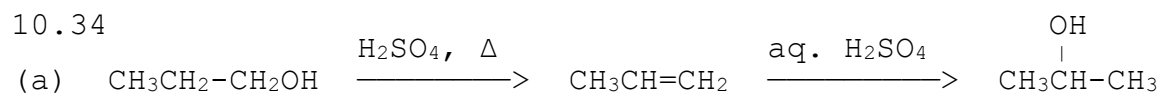
(e) e.g., 3-bromo-2-propoxy-2-butanol:
$$\begin{array}{c} \text{Br} \quad \text{OH} \\ | \quad | \\ \text{CH}_3\text{CHCCH}_3 \\ | \\ \text{OCH}_2\text{CH}_2\text{CH}_3 \end{array}$$

10.29 With more (2) Hs on its O, water has more hydrogen "bonds" per molecule.

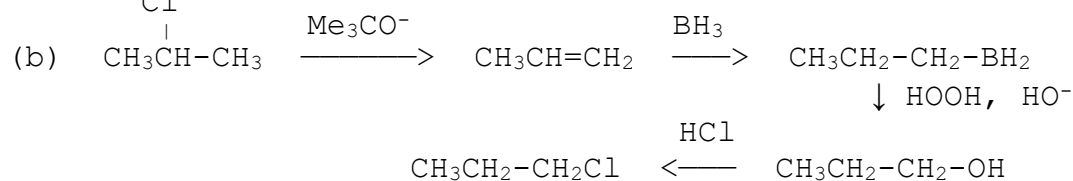
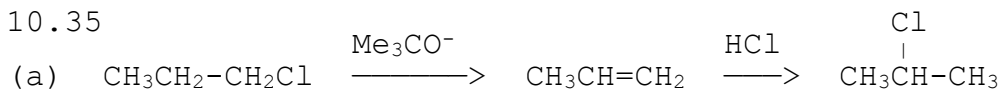
10.30 It has only 2 Cs per O functional group so it is very soluble in water.



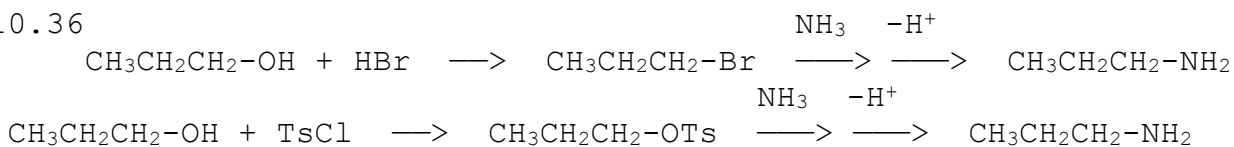
(b) In the first step the protic solvent methanol helps the alkyl halide ionize. In the second step methanol is the nucleophile. In the third step methanol is the base.



10.35



10.36



10.37 (a) $\text{CH}_3\text{CH}_2\text{OH}_2^+$ (b) $\text{CH}_3\text{CH}_2\text{OTs}$ (c) $\text{CH}_3\text{CH}_2\text{O}^-$ (d) $\text{CH}_3\text{CH}_2\text{Br}$ (e) $\text{CH}_3\text{CO}_2\text{H}$
 (f) $\text{CH}_3\text{CH}_2\text{O}^-$ (g) $\text{CH}_3\text{CH}_2\text{Cl}$ (h) $\text{CH}_3\text{CH}=\text{O}$ (i) $\text{CH}_3\text{CH}_2\text{O}^-$ (j) no rx. (k) $\text{CH}_2=\text{CH}_2$
 (l) $\text{CH}_3\text{CH}_2\text{Br}$ (m) $\text{CH}_3\text{CH}_2\text{O}^-$ (n) $\text{CH}_3\text{CO}_2\text{H}$

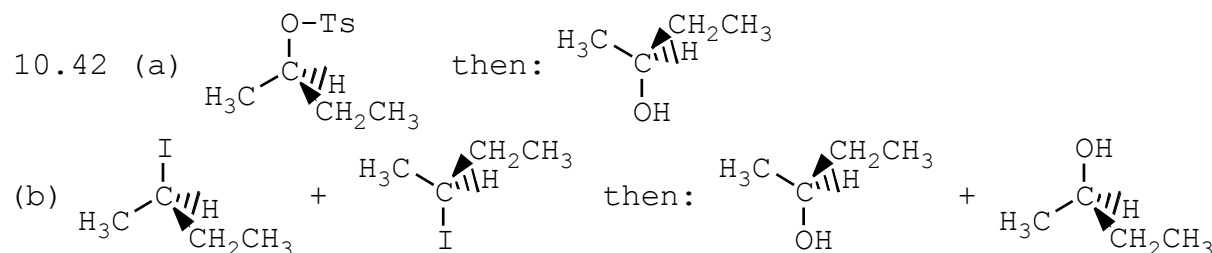
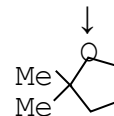
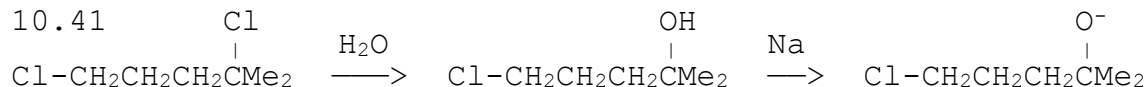
10.38 (a) $\text{Me}_2\text{CHOH}_2^+$ (b) Me_2CHOTs (c) Me_2CHO^- (d) Me_2CHBr (e) $\text{Me}_2\text{C}=\text{O}$ (f) Me_2CO^-
 (g) Me_2CCl (h) $\text{Me}_2\text{C}=\text{O}$ (i) Me_2CO^- (j) no rx. (k) $\text{CH}_3\text{CH}=\text{CH}_2$ (l) Me_2CHBr
 (m) Me_2CHO^- (n) $\text{Me}_2\text{C}=\text{O}$

10.39 (a) $\text{Me}_3\text{COH}_2^+$ (b) Me_3COTs (c) Me_3CO^- (d) Me_3CBr (e) no rx. (f) Me_3CO^-
 (g) Me_3CCl (h) no rx. (i) Me_3CO^- (j) no rx. (k) $\text{Me}_2\text{C}=\text{CH}_2$ (l) Me_3CBr (m) Me_3CO^-
 (n) no rx.

10.40 (a) $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$ (b) $\text{CH}_3\text{CH}_2\text{OH} + \text{BrCH}_2\text{CH}_2\text{O}^-$

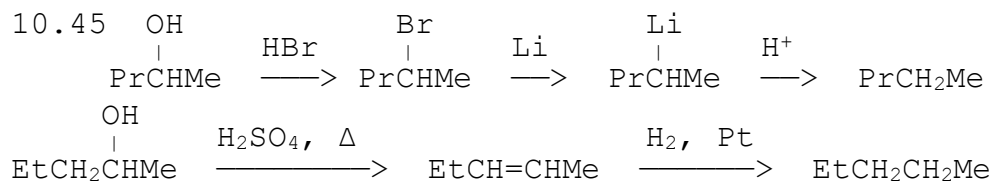
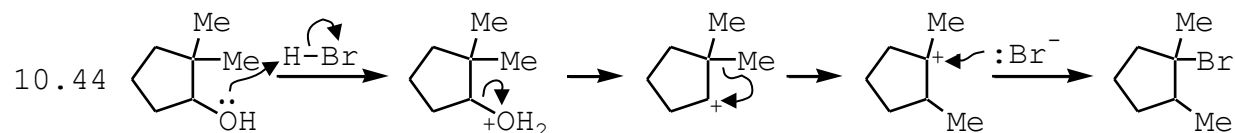
(c) Yes. In basicity: $\text{Br-CH}_2\text{CH}_2\text{O}^- < \text{CH}_3\text{CH}_2\text{O}^-$ because δ^+ from χ Br attracts & stabilizes base e⁻s. Survival of the weakest.

(d) acid-base reaction is faster (acid-base reactions are generally very fast)

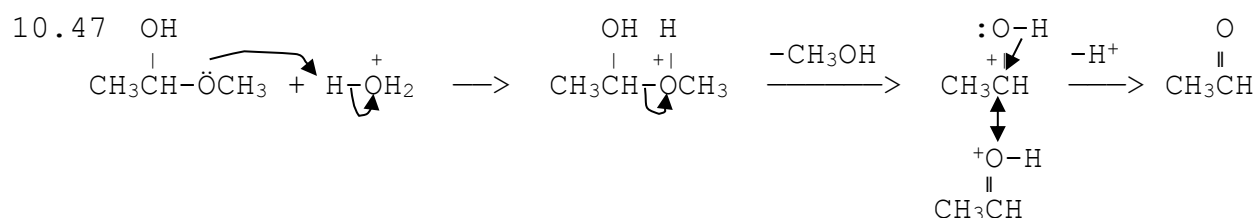


(c) The tosylate, formed with retention of configuration, inverts during $\text{S}_{\text{N}}2$ with HO^- . The 2 iodide enantiomers, formed by $\text{S}_{\text{N}}1$ with retention and inversion, both invert during $\text{S}_{\text{N}}2$ with HO^- .

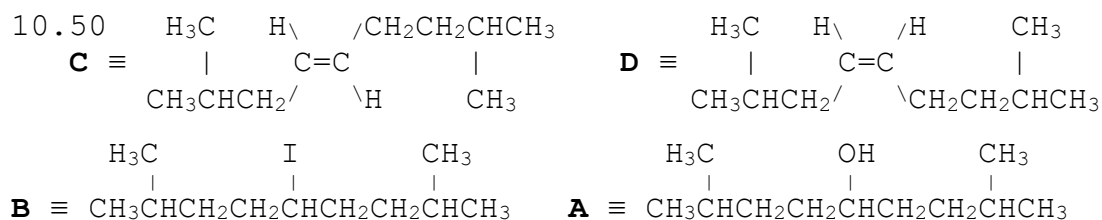
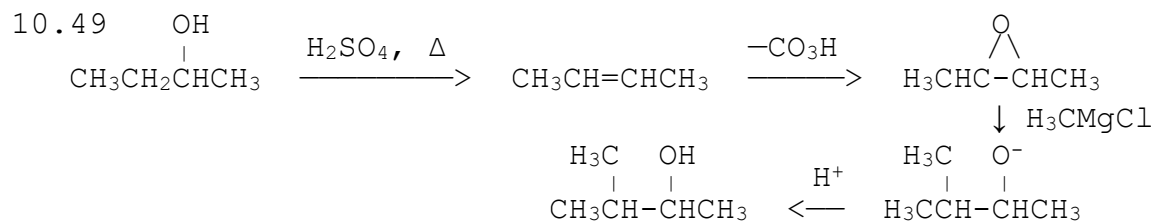
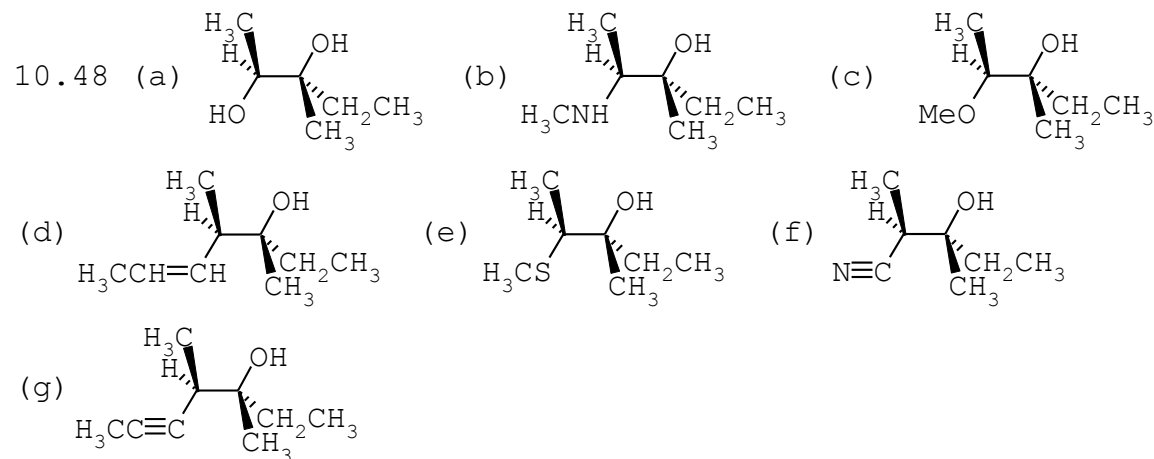
10.43 With hydroxide it can only exchange a proton. With aqueous sulfuric acid it can undergo S_N1 hydrolysis with equal amounts of retention and inversion of configuration.

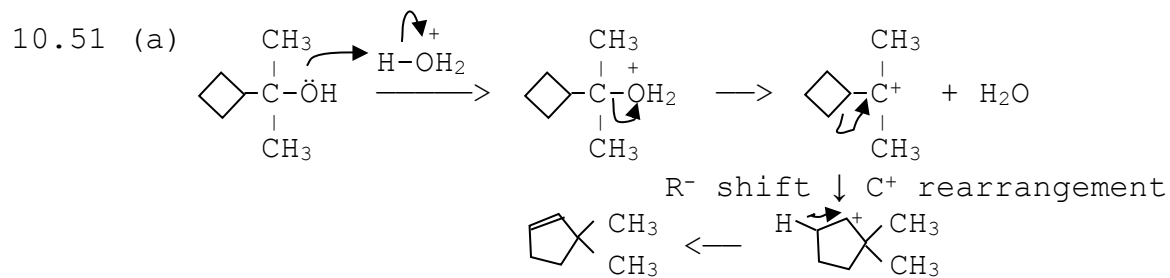


10.46 (a) no reaction (b) ⁻O-CH₂-CH₂-OH (by S_N2)



This reaction goes easily because resonance stabilizes the C⁺.





(b) A 3°C^+ becomes a 2°C^+ , normally less stable. With much less ring strain, the 2°C^+ is stabler.

10.52 (a) Cl^- (b) SOCl_2 (c) HCl (with C^+ rearrangement)

10.53 (a) $\text{CH}_3\text{CH}_2\text{OH}_2\text{-Br}$; not feasible because 10 e's surround O.

(b) $\text{CH}_3\text{CH}_2\text{OH}^+-\text{Br} + \text{H}^-$; or $\text{Br}^+-\text{OH}_2 + \text{CH}_3\text{CH}_2^-$; neither is feasible because H^- and CH_3CH_2^- are both very strong bases & awful Ls

10.54 (a) A large alcohol with more than 5 Cs per O functional group.

(b) The insoluble alkyl chloride corresponding to the alcohol.

10.55 Methyl, primary, and secondary alcohols because they can be oxidized by Cr(VI) .