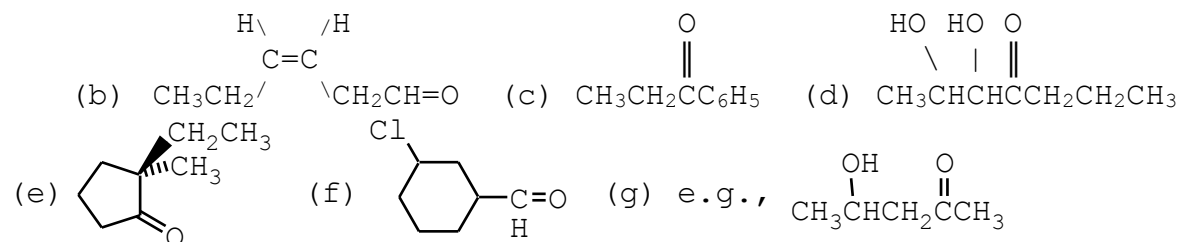


Answers to Puzzles of Chapter 12
Aldehydes and Ketones

12.1 4 stereoisomers because it has 2 chiral atoms.

12.2 (a) butanal (b) 1-penten-3-one (c) 1,1-dibromopropanone (d) cyclobutanone
(e) 1-cyclobutylethanone (f) cyclobutanecarbaldehyde (g) phenylethanal
(h) benzenecarbaldehyde (i) hydroxyethanal (j) 3-hexyne-2,5-dione

12.3 (a) $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}=\text{O}$



12.4 in bp: 2-butanol > 2-butanone > propanone because only 2-butanol has H "bonds", and because 2-butanone is larger and has more dispersion forces than propanone.

12.5 in water solubility: pentanedial > pentanal > hexanal because pentanedial has two polar aldehyde groups, and because pentanal has fewer carbons and more polarity than hexanal.

12.6 (a) $\text{CH}_3(\text{CH}_2)_{10}\text{OH} + \text{anhyd. Cr(VI)} \longrightarrow \text{CH}_3(\text{CH}_2)_9\text{CH}=\text{O}$

(b) $\text{CH}_3(\text{CH}_2)_{10}\text{Br} + \text{HO}^- \longrightarrow \text{CH}_3(\text{CH}_2)_{10}\text{OH}$, then part (a)

(c) $\text{CH}_3(\text{CH}_2)_8\text{CH}=\text{CH}_2 \xrightarrow{1. \text{BH}_3 \quad 2. \text{HOOH}, \text{HO}^-} \text{CH}_3(\text{CH}_2)_{10}\text{OH}$, then part (a)

(d) $\text{CH}_3(\text{CH}_2)_8\text{C}\equiv\text{CH} \xrightarrow{1. \text{BH}_3 \quad 2. \text{HOOH}, \text{HO}^-} \text{CH}_3(\text{CH}_2)_9\text{CH}=\text{O}$

(e) $\text{CH}_3(\text{CH}_2)_8\text{OH} \xrightarrow{\text{HBr}} \text{CH}_3(\text{CH}_2)_8\text{Br} \xrightarrow{\text{Li}} \text{CH}_3(\text{CH}_2)_8\text{Li} \xrightarrow{\text{H}_2\text{C}=\text{CH}_2} \text{CH}_3(\text{CH}_2)_{10}\text{O}^- \xrightarrow{\text{H}^+} \text{CH}_3(\text{CH}_2)_{10}\text{OH} \xrightarrow{\text{anhyd. Cr(VI)}} \text{CH}_3(\text{CH}_2)_9\text{CH}=\text{O}$

12.7 (a) $\begin{array}{c} \text{OH} \quad \text{OH} \\ | \quad | \\ \text{CH}_3\text{CHCH}_2\text{CH}_2\text{CHCH}_3 \end{array} \xrightarrow{\text{Cr(VI)}} \begin{array}{c} \text{O} \quad \text{O} \\ || \quad || \\ \text{CH}_3\text{CCH}_2\text{CH}_2\text{CCH}_3 \end{array}$

(b) $\square \square \xrightarrow{1. \text{O}_3 \quad 2. \text{Zn}} \uparrow$

(c) $\begin{array}{c} \text{CH}_3\text{CCH}_2\text{CH}_2\text{CCH}_3 \\ || \quad || \\ \text{O} \quad \text{O} \end{array} \xrightarrow{1. \text{O}_3 \quad 2. \text{Zn}} 2 \begin{array}{c} \text{O} \quad \text{O} \\ || \quad || \\ \text{CH}_3\text{CCH}_2\text{CH}_2\text{CCH}_3 \end{array}$

(d) $\text{HC}\equiv\text{CCH}_2\text{CH}_2\text{C}\equiv\text{CH} + \text{aq. H}_2\text{SO}_4 + \text{Hg}^{2+} \longrightarrow \text{product}$

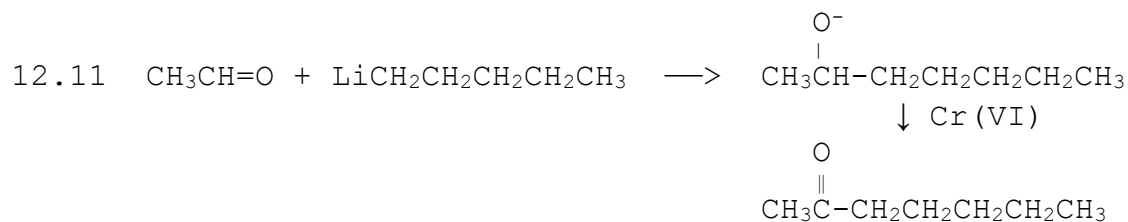
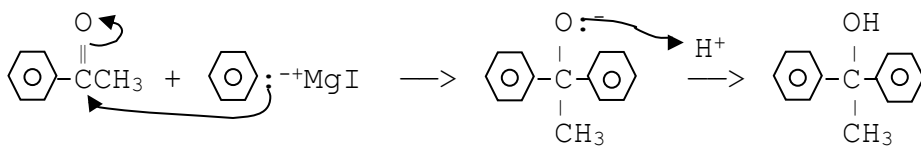
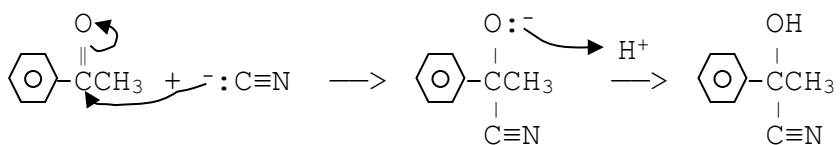
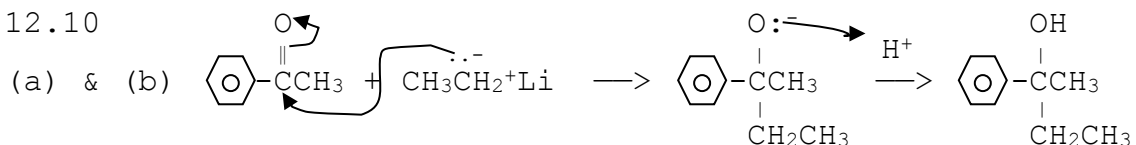
12.8 in reactivity: $\begin{array}{c} \text{HO} \quad \text{O} \\ | \quad || \\ \text{CH}_3\text{CHCH} \\ \delta^+ \quad \delta^+ \end{array} > \begin{array}{c} \text{O} \\ || \\ \text{CH}_3\text{CH}_2\text{CH} \end{array} > \begin{array}{c} \text{O} \\ || \\ \text{CH}_3\text{CCH}_3 \end{array} > \begin{array}{c} \text{O} \\ || \\ \text{CH}_3\text{CH}_2\text{CCH}_2\text{CH}_3 \end{array}$

The HO group puts a δ^+ on a C, which repels & destabilizes the carbonyl carbon's δ^+ . Aldehydes are sterically and electronically more electrophilic than ketones. A smaller ketone is less sterically hindered than a larger ketone.

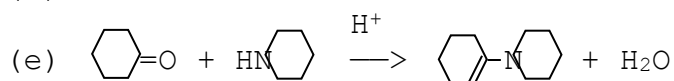
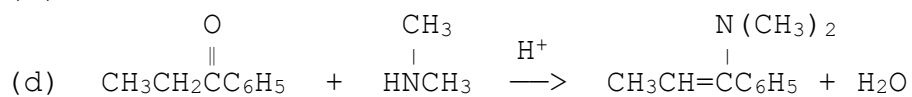
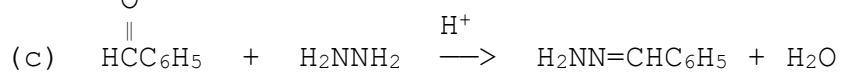
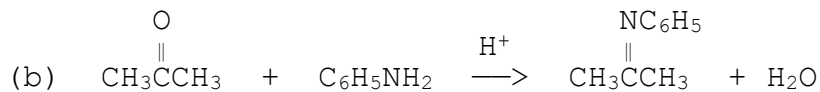
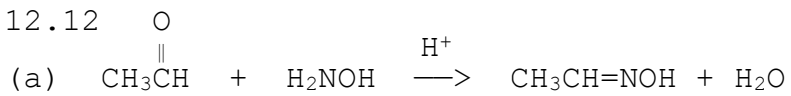
12.9 (a) 180° (b) The *sp* C because it has a large δ^+ and it is sterically open.

(c) Faster with methyl isocyanate because its *sp* C has more δ^+ .

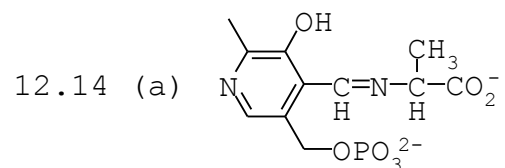
12.10

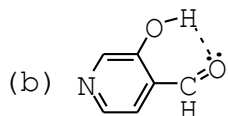


12.12

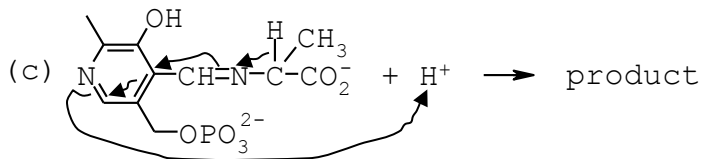


12.13 $(\text{HOCH}_2)_2\text{C}=\text{N}-\text{R}$

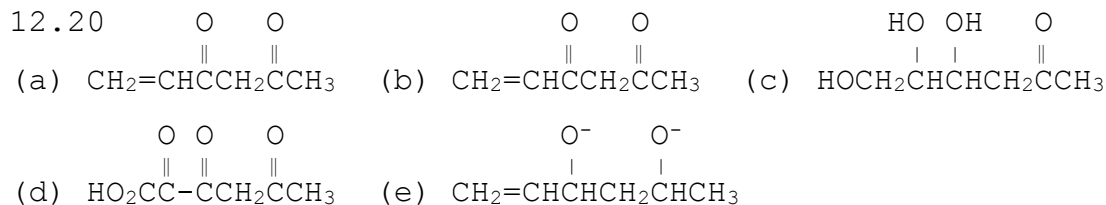
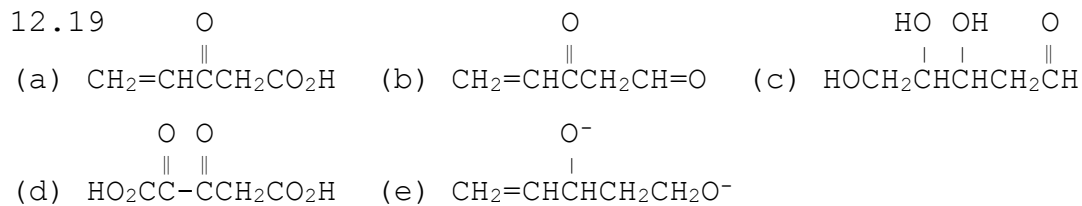
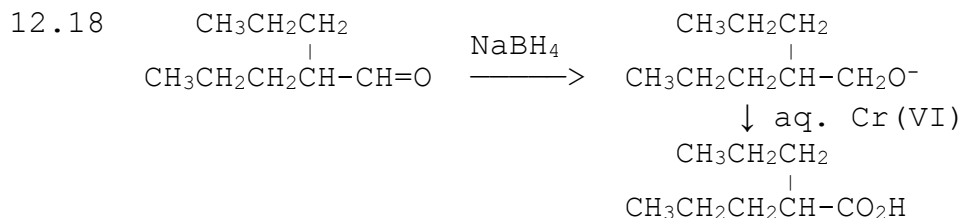
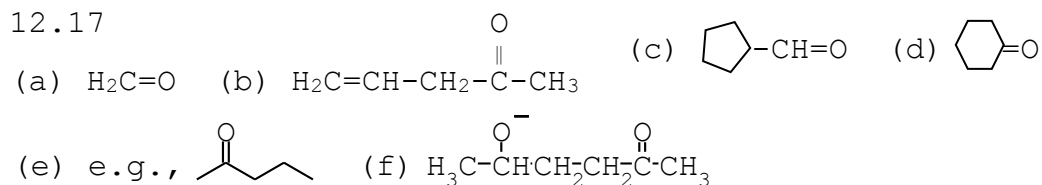
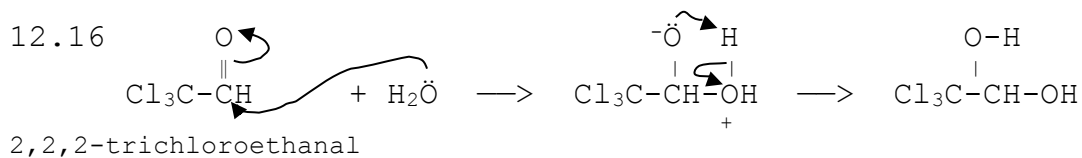
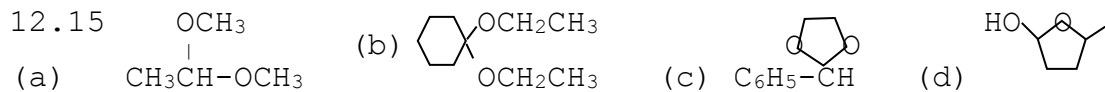


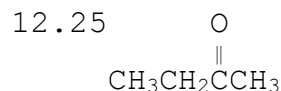
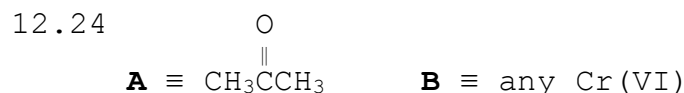
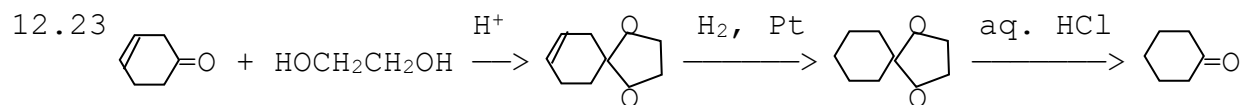
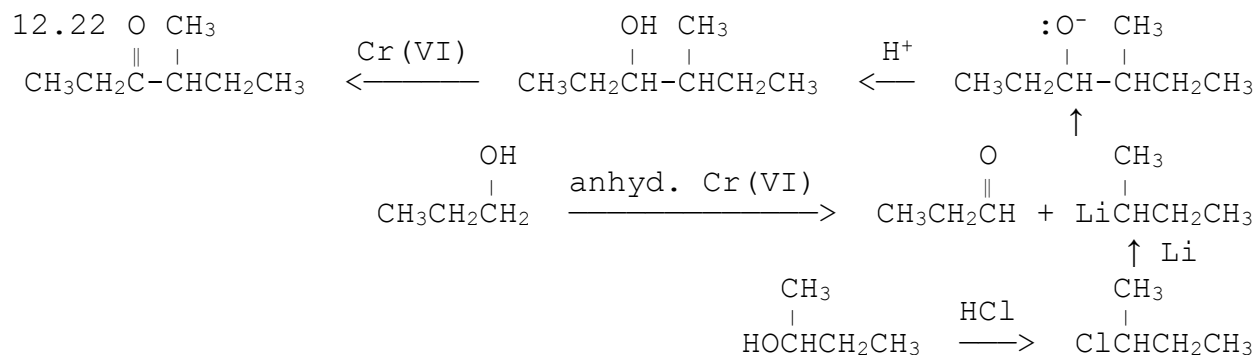
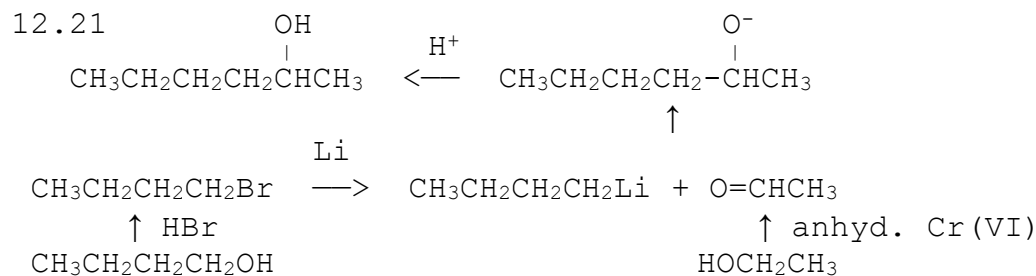


The intramolecular H "bond" ↓ e⁻ density & ↑ electrophilicity of the C=O.



(d) The addition of an amine to a ketone.





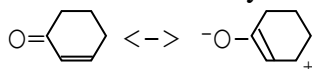
$((2 \cdot 4 + 2) - 8) / 2 = 1$ π bond or ring. According to C=O in the IR, 1 π bond, no ring.

IR: $3000\text{-}2850\text{ cm}^{-1}$ (s): sp^3 C-H; 1720 cm^{-1} (s): C=O

no bands at $2840\text{-}2700\text{ cm}^{-1}$ means that the carbonyl is a ketone, not an aldehyde.

NMR: δ 2.4(q): CH₂; δ 2.1 (s): CH₃C=O; δ 1.0 (t): CH₃CC=O

12.26 1700 cm^{-1} : acyclic C=O; 1660 cm^{-1} : cyclic C=O because resonance weakens C=O:



12.27 (a) 3-pentynal (b) (*E*)-4-hexen-3-one (c) (*S*)-2-methyl-3-hydroxypropanal
(d) 1-chloro-3-cyclopentylpropanone

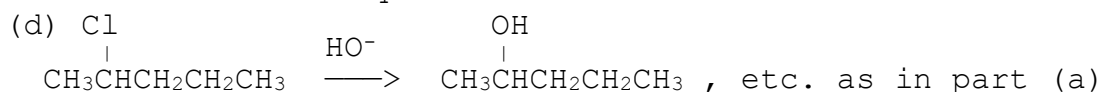
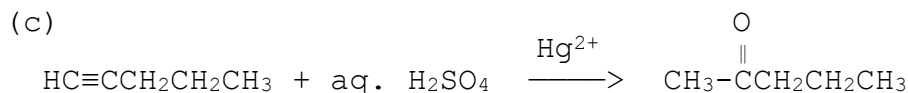
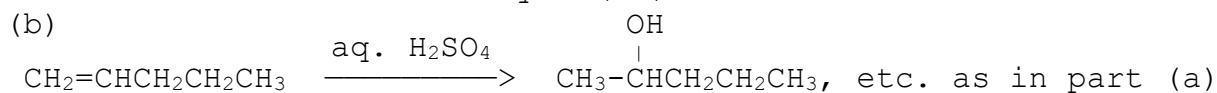
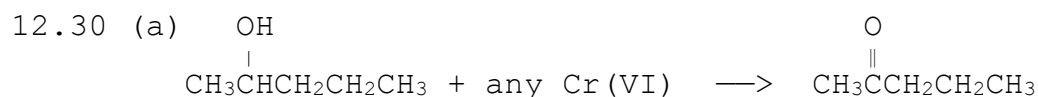
12.28 (a) 2-iodopropanal: $\text{CH}_3\text{CHI-CH=O}$

(b) 2,5-heptanedione: $\text{CH}_3\overset{\text{O}}{\parallel}\text{CCH}_2\text{CH}_2\overset{\text{O}}{\parallel}\text{CCH}_2\text{CH}_3$

(c) 2-pentanone: $\text{CH}_3\overset{\text{O}}{\parallel}\text{CCH}_2\text{CH}_2\text{CH}_3$

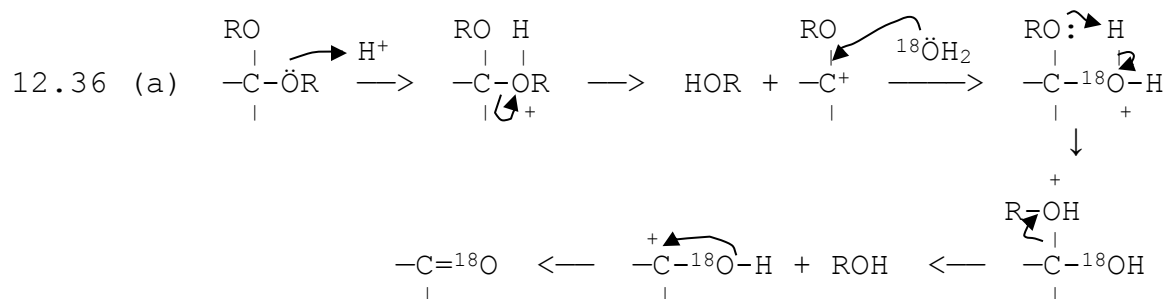
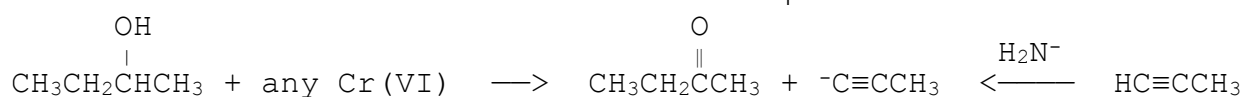
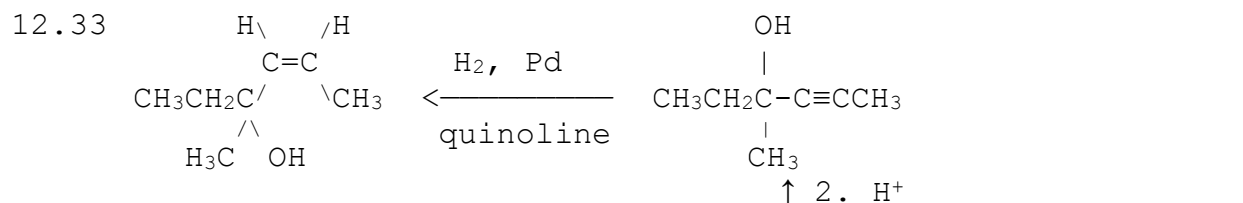
(d) 4-hydroxy-2-butanone: $\text{HOCH}_2\text{CH}_2\overset{\text{O}}{\parallel}\text{CCH}_3$

12.29 The 3- isomer has the wrong geometry for an intramolecular H "bond", so its HO and carbonyl O are free to form intermolecular H "bonds", which raise the bp. The 2- isomer can form an intramolecular H "bond", so it is less free to form intermolecular H "bonds".



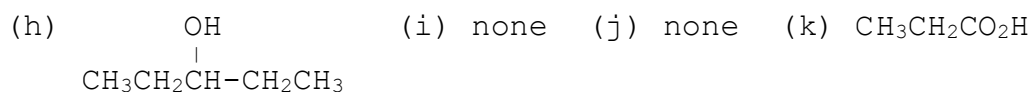
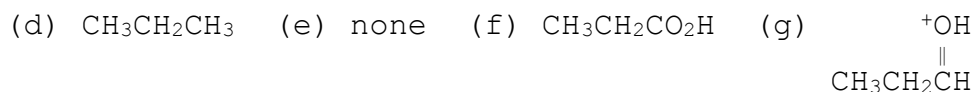
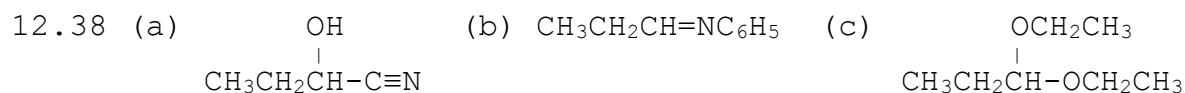
12.31 e.g., bp, dipole moment, density, refractive index, NMR spectroscopy

12.32 The elimination reactions are impossible because the H^- and R^- are extremely basic and impossible leaving groups.



(b) in the carbonyl compound

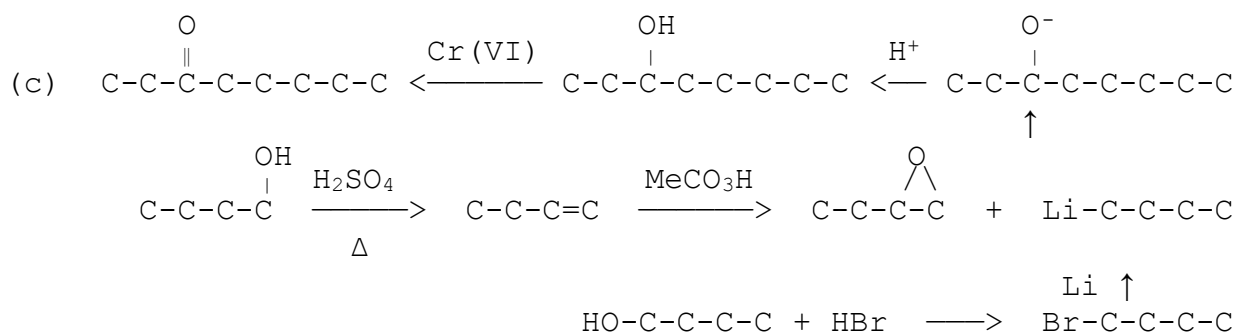
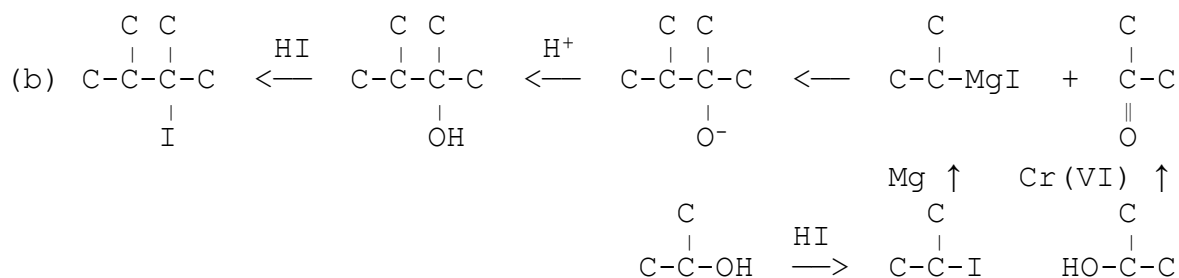
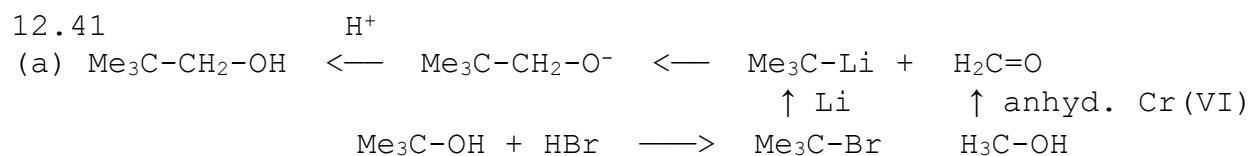
12.37 H_2NNH_2 , HO^- (avoid acidic conditions of Zn, HCl)



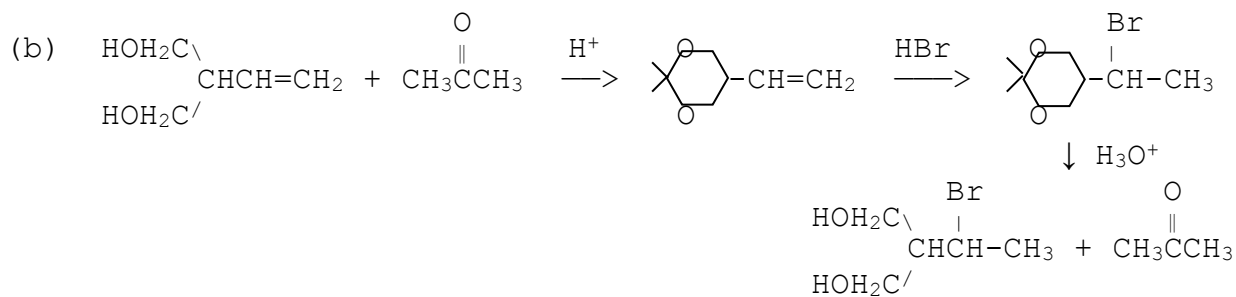
- (l) $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ (m) none (n) $\text{CH}_3\text{CH}_2\overset{\text{O}^-}{\text{C}}\text{H}-\text{C}\equiv\text{CCH}_3$
 (o) $\text{CH}_3\text{CH}=\text{CH}-\text{N}(\text{CH}_3)_2$ (p) $\text{CH}_3\text{CH}_2\text{CH}_3$ (q) none (r) $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$
 (s) $\text{CH}_3\text{CH}_2\text{CO}_2\text{H}$ (t) $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$

- 12.39 (a) $(\text{CH}_3)_2\overset{\text{OH}}{\text{C}}-\text{C}\equiv\text{N}$ (b) $(\text{CH}_3)_2\text{C}=\text{NC}_6\text{H}_5$ (c) $(\text{CH}_3)_2\overset{\text{OCH}_2\text{CH}_3}{\text{C}}-\text{OCH}_2\text{CH}_3$
 (d) $\text{CH}_3\text{CH}_2\text{CH}_3$ (e) none (f) none (g) $\text{CH}_3\overset{+\text{OH}}{\underset{\parallel}{\text{C}}}\text{CH}_3$
 (h) $(\text{CH}_3)_2\overset{\text{OH}}{\text{C}}-\text{CH}_2\text{CH}_3$ (i) none (j) none (k) none (l) $(\text{CH}_3)_2\text{CHOH}$
 (m) none (n) $(\text{CH}_3)_2\overset{\text{O}^-}{\text{C}}-\text{C}\equiv\text{CCH}_3$ (o) $\text{CH}_2=\overset{\text{CH}_3}{\text{C}}-\text{N}(\text{CH}_3)_2$ (p) $\text{CH}_3\text{CH}_2\text{CH}_3$
 (q) none (r) $(\text{CH}_3)_2\text{CHOH}$ (s) none (t) $(\text{CH}_3)_2\text{CHOH}$

- 12.40 (a) With 7 C's/ O group they are not polar enough to dissolve well in water.
 (b) By protonating their O's and making them ionic and polar, 50% H_2SO_4 does dissolve them.



- 12.42 (a) an acetal with propanone

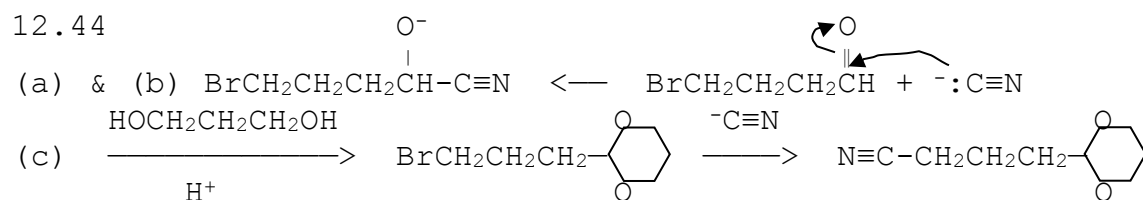


12.43 $(\text{CH}_3)_2\text{CHCH}=\text{O}$

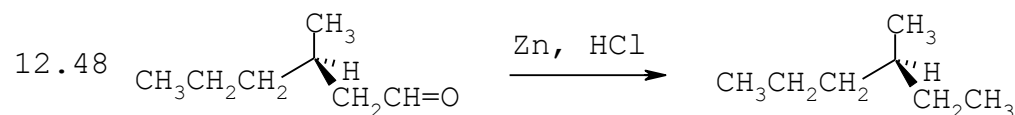
$((2 \cdot 4 + 2) - 8) / 2 = 1 \pi$ bond or ring

IR: $3000\text{-}2850 \text{ cm}^{-1}$ (s): sp^3 C-H; $2800, 2710 \text{ cm}^{-1}$ (m): O=C-H; 1740 cm^{-1} (s): O=C

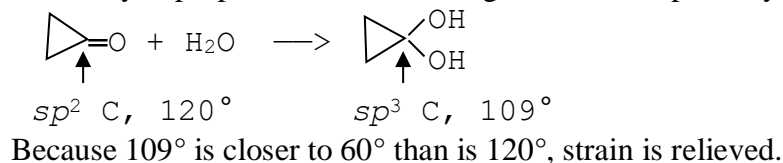
NMR: δ 9.6 (d): O=CH; δ 2.4 (multiplet): CH-C=O; δ 1.1 (d): CH_3



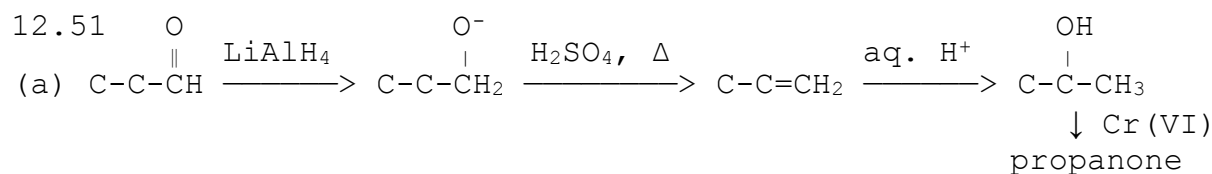
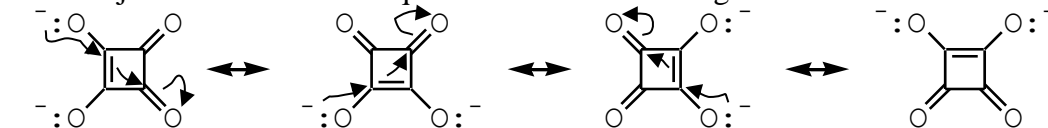
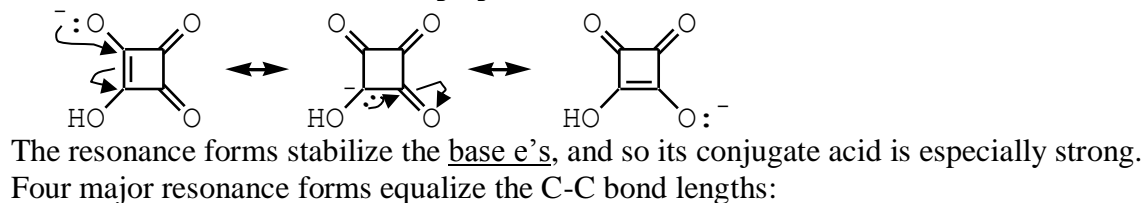
12.45 Propanal because it is less stable but gives the same products as the ketone.

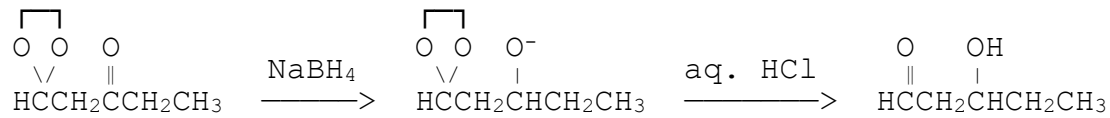
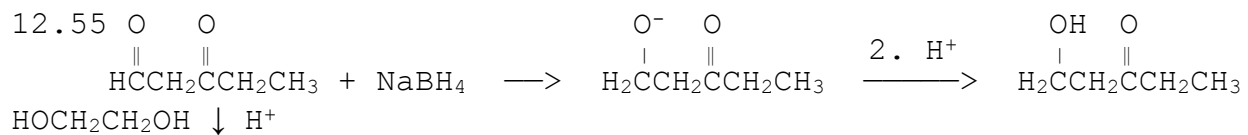
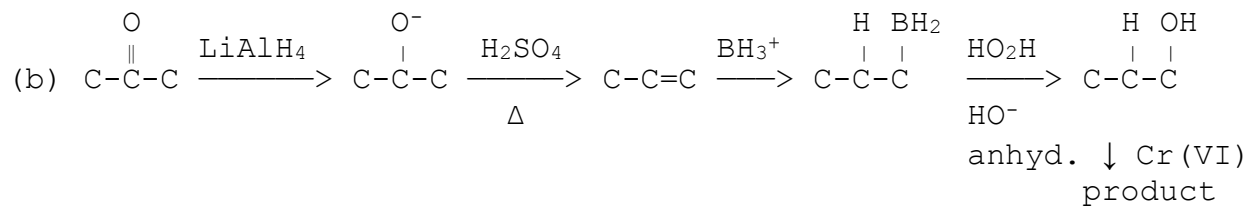


12.49 Cyclopropanone has much ring strain that is partially relieved upon hydration:



12.50 Examine the conjugate base:





6/05