1. (5 pts. each, 50 pts. total) Draw the major product of each of the following reactions. Be sure to indicate the stereochemistry of the product, if appropriate.

(a) \[
\begin{align*}
\text{H}_3\text{C} & - \text{CH}_3 \\
\text{H}_3\text{C} & - \text{CH}_3
\end{align*}
\quad \xrightarrow{\text{HBr, peroxides}}
\quad \begin{align*}
\text{H}_3\text{C} & - \text{CH}_3 \\
\text{Br}
\end{align*}
\]

(b) \[
\begin{align*}
\text{H}_3\text{C} & - \text{CH}_3 \\
\text{H}_3\text{C} & - \text{CH}_3
\end{align*}
\quad \xrightarrow{\text{BH}_3, \text{base}}
\quad \begin{align*}
\text{H}_3\text{C} & - \text{CH}_3 \\
\text{OH}
\end{align*}
\]

(c) \[
\begin{align*}
\text{MeO} & - \text{O} \\
\text{MeO} & - \text{H}
\end{align*}
\quad +
\quad \text{O}_\text{C} = \text{CH}_2
\quad \xrightarrow{\Delta}
\quad \begin{align*}
\text{MeO} & - \text{O} \\
\text{H}
\end{align*}
\]

(d) \[
\begin{align*}
\text{H}_3\text{C} & - \text{CH}_3 \\
\text{H}_3\text{C} & - \text{CH}_3
\end{align*}
\quad \xrightarrow{\text{cat. TsOH}}
\quad \begin{align*}
\text{H}_3\text{C} & - \text{CH}_3 \\
\text{CH}_3
\end{align*}
\]

(e) \[
\begin{align*}
\text{H}_3\text{C} & - \text{O}_\text{C}
\end{align*}
\quad \xrightarrow{\text{O}_2}
\quad \begin{align*}
\text{H}_3\text{C} & - \text{OO}
\end{align*}
\]
(f) \[
\begin{array}{c}
\text{CH}_3 \\
\text{CH}_3 \\
\text{CH}_3 \\
\text{CH}_3 \\
\text{CH}_3 \\
\text{CH}_3 \\
\text{CH}_3 \\
\text{CH}_3 \\
\end{array}
\xrightarrow{\text{NBS, MeOH}}
\begin{array}{c}
\text{CH}_3 \\
\text{CH}_3 \\
\text{CH}_3 \\
\text{CH}_3 \\
\text{CH}_3 \\
\text{CH}_3 \\
\text{CH}_3 \\
\text{CH}_3 \\
\end{array}
\]

(g) \[
\begin{array}{c}
\text{CH}_3 \\
\text{CH}_3 \\
\text{CH}_3 \\
\text{CH}_3 \\
\text{CH}_3 \\
\text{CH}_3 \\
\text{CH}_3 \\
\text{CH}_3 \\
\end{array}
\xrightarrow{\text{H}_2\text{O, cat. H}_2\text{SO}_4, \text{cat. HgSO}_4}
\begin{array}{c}
\text{CH}_3 \\
\text{CH}_3 \\
\text{CH}_3 \\
\text{CH}_3 \\
\text{CH}_3 \\
\text{CH}_3 \\
\text{CH}_3 \\
\text{CH}_3 \\
\end{array}
\]

(h) \[
\begin{array}{c}
\text{Ph} \\
\text{OTs} \\
\text{O} \\
\text{O} \\
\text{O} \\
\text{O} \\
\text{O} \\
\text{O} \\
\end{array}
\xrightarrow{\text{EtSK}}
\begin{array}{c}
\text{Ph} \\
\text{SEt} \\
\text{O} \\
\text{O} \\
\text{O} \\
\text{O} \\
\text{O} \\
\text{O} \\
\end{array}
\]

(i) \[
\begin{array}{c}
\text{H}_3\text{C} \\
\text{CH}_3 \\
\text{O} \\
\text{O} \\
\text{O} \\
\text{O} \\
\text{O} \\
\text{O} \\
\end{array}
\xrightarrow{\text{O}_3, \text{then Me}_2\text{S}}
\begin{array}{c}
\text{O} \\
\text{O} \\
\text{O} \\
\text{O} \\
\text{O} \\
\text{O} \\
\text{O} \\
\text{O} \\
\end{array}
\]

(j) \[
\begin{array}{c}
\text{H}_3\text{C} \\
\text{CH}_3 \\
\text{CH}_3 \\
\text{CH}_3 \\
\text{CH}_3 \\
\text{CH}_3 \\
\text{CH}_3 \\
\text{CH}_3 \\
\end{array}
\xrightarrow{\text{CH}_2\text{I}_2, \text{Zn}}
\begin{array}{c}
\text{H}_3\text{C} \\
\text{CH}_3 \\
\text{CH}_3 \\
\text{CH}_3 \\
\text{CH}_3 \\
\text{CH}_3 \\
\text{CH}_3 \\
\text{CH}_3 \\
\end{array}
\]
2. (45 pts. total) Design syntheses of each of the following compounds from the indicated starting materials. Show all reagents required for each transformation. You are advised to conduct a retrosynthetic analysis before working in the forward direction. Each synthesis will require more than one step.

(a) (10 pts.)

Retro:

Forward:

(b) (15 pts.)

Retro:

Forward:
(c) (10 pts.)

\[
\begin{align*}
\text{H}_3\text{C} & \xrightarrow{\text{OH}} \text{CH}_3 \xrightarrow{\text{Br}} \text{H}_3\text{C} \\
\text{Br} & \xrightarrow{\text{OH}} \text{CH}_3 & \text{CH}_3 & \xrightarrow{\text{an alkyne}} & \\
\end{align*}
\]

Retro:

\[
\begin{align*}
\text{H}_3\text{C} & \equiv \text{CH}_3 \\
\text{OH} & \equiv \text{CH}_3 \xrightarrow{\text{Br}} \text{H}_3\text{C} & \text{CH}_3 & \xrightarrow{\text{H}_3\text{C} \equiv \text{CH}_3} & \\
\text{Br} & \equiv \text{CH}_3 & \text{OH} & \equiv \text{CH}_3 & \\
\end{align*}
\]

Forward:

\[
\begin{align*}
\text{H}_3\text{C} & \equiv \text{CH}_3 \xrightarrow{\text{Na} \text{ liquid NH}_3} \text{H}_3\text{C} & \equiv \text{CH}_3 & \xrightarrow{\text{NBS} \text{ H}_2\text{O}} \text{H}_3\text{C} & \equiv \text{OH} \\
\text{Br} & \equiv \text{CH}_3 & \equiv \text{Br} & \equiv \text{CH}_3 & \\
\end{align*}
\]

(d) (10 pts.)

\[
\begin{align*}
\text{CH}_3 & \equiv \text{CN} \xrightarrow{\text{an alkene with fewer C atoms}} & \\
\end{align*}
\]

Retro:

\[
\begin{align*}
\text{CH}_3 & \equiv \text{CN} \\
\equiv \text{CH}_3 & \equiv \text{CH}_3 & \equiv \text{CH}_3 & \equiv \text{CH}_3 & \\
\equiv \text{CH}_3 & \equiv \text{Br} & \equiv \text{Br} & \equiv \text{CH}_3 & \\
\end{align*}
\]

Forward:

\[
\begin{align*}
\text{CH}_3 & \equiv \text{CN} \xrightarrow{\text{HBr} \text{ air}} \text{CH}_3 & \equiv \text{CN} & \equiv \text{CN} \\
\equiv \text{CH}_3 & \equiv \text{Br} & \equiv \text{Br} & \equiv \text{CN} & \\
\equiv \text{CH}_3 & \equiv \text{Br} & \equiv \text{Br} & \equiv \text{CN} & \\
\equiv \text{CH}_3 & \equiv \text{CN} & \equiv \text{CN} & \equiv \text{CN} & \\
\end{align*}
\]
3. (65 pts. total) Draw reasonable mechanisms for each of the following reactions. Use the curved arrow convention to show the movement of electrons. *Remember to obey Grossman’s Rule!*

(a) (25 pts.)

Initiation:

\[
\begin{align*}
\text{Br}_2 & \rightarrow \cdot \text{Br} \\
\text{Br--Br} & \rightarrow \cdot \text{Br}
\end{align*}
\]

Propagation:

\[
\begin{align*}
\text{H} & \text{H} \\
\cdot \text{Br} & \rightarrow \cdot \text{Br} \\
\text{H} & \text{H} \\
\cdot \text{Br} & \rightarrow \cdot \text{Br}
\end{align*}
\]
(b) (20 pts.)

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{H}_2\text{SO}_4 \\
\text{H}_3\text{C} & \quad \text{O} \\
\text{H}_3\text{C} & \quad \text{OH} \\
\text{H}_3\text{C} & \quad \text{OH} \\
\end{align*}
\]
(c) (20 pts.)

\[
\begin{align*}
\text{EtOH} & \quad \xrightarrow{\text{cat. EtO}^-} \quad \text{EtO}^- \\
& \quad \xrightarrow{\text{EtO}^-} \\
& \quad \xrightarrow{\text{EtO}^-} \\
& \quad \xrightarrow{\text{EtO}^-} \\
& \quad \xrightarrow{\text{EtO}^-} \\
& \quad \xrightarrow{\text{EtO}^-} \\
\end{align*}
\]
4. (5 pts. each, 40 pts. total) Explain each of the following observations in no more than one or two short, easily understood sentences.

(a) Ethyl $t$-butyl ether is much more prone to undergo autoxidation than is methyl $t$-butyl ether.

\[
\begin{align*}
\text{ethyl } t\text{-butyl ether} & \quad \begin{array}{c}
\text{methyl } t\text{-butyl ether}\\
\end{array} \\
\end{align*}
\]

Abstraction of H from the OCH$_2$ group in ETBE gives a much lower energy radical than abstraction of H from the OCH$_3$ group in MTBE, so ETBE undergoes autoxidation more quickly.

(b) Even though the two large groups are on the same side of the ring in the cis compound, the cis compound is \textit{lower in energy} than the trans compound.

\[
\begin{align*}
\text{cis} & \quad \text{trans} \\
\end{align*}
\]

In their lowest energy chair conformations, the first compound has both large groups equatorial, whereas the second compound has one large group axial and one equatorial. The former arrangement is much lower in energy.
(c) The Diels–Alder reaction shown below does not proceed at all.

\[
\begin{array}{c}
\text{H}_3\text{C} \\
\text{O} \\
\text{CH}_3 \\
\end{array} \quad \text{O} \quad \text{CH}_3 \\
\text{H}_3\text{C} \quad \text{O} \\
\text{CH}_3 \\
\text{O}
\]

The D–A reaction requires that one of the components (usually the dienophile) be electron-poor, and the other (usually the diene) be electron-rich. If both the diene and the dienophile have electron-withdrawing groups attached, as in the situation above, the reaction will not proceed.

(d) When the enantiopure tosylate shown below is allowed to react with NaCN, one optically active and one optically inactive product is obtained.

\[
\begin{array}{c}
\text{OTs} \\
\text{OTs} \\
\text{OTs} \\
\text{OTs} \\
\text{OTs}
\end{array}
\]

The \( S_N2 \) product is chiral, and this reaction proceeds with clean inversion, so the product is optically active. An \( S_N2' \) product is also obtained, but it is achiral, so it is optically inactive.
(e) Even though O is very electronegative, carbocations are strongly stabilized by an O atom directly attached to the electron-deficient C atom.

\[
\text{MeO}^+ + \underset{\text{CH}_3}{\text{CH}_3} \quad \text{is lower in energy than} \quad \text{H}_3\text{C}^+ + \underset{\text{CH}_3}{\text{CH}_3}
\]

The O atom is a resonance donor, and it can stabilize carbocations by sharing its lone pair.

(f) More substituted radicals are lower in energy than less substituted radicals. (An orbital energy diagram would be helpful here.)

\[
\text{H}_3\text{C}^\cdot + \underset{\text{CH}_3}{\text{CH}_3} \quad \text{is lower in energy than} \quad \text{H}_3\text{C}^\cdot + \underset{\text{CH}_2}{\text{CH}_2}
\]

Hyperconjugative stabilization of the radical occurs.

\[
\text{C}(\text{sp}^2) \quad \text{C}(\text{sp}^3) - \text{H}
\]

Two electrons decline in energy, one increases in energy, so the net result is stabilization.
(g) A conjugated 1,3-diene absorbs light of longer wavelengths (lower energy) than a regular alkene.

\[
\text{\[
\begin{array}{c}
\text{\[
\begin{array}{c}
\psi_3 \\
\psi_2 \\
\psi_1 \\
\psi_0
\end{array}
\end{array}
\text{ decreased HOMO-LUMO gap in diene}
\end{array}
\text{\[
\begin{array}{c}
\pi^* \\
\pi^*
\end{array}
\end{array}
\text{ absorbs longer wavelengths than }
\begin{array}{c}
\pi \\
\pi
\end{array}
\end{array}
\right]
\]}
\]
\]

(h) The S atom is HS\(^{-}\) is a worse base and a better nucleophile than the O atom in HO\(^{-}\).
(Note: Merely citing the position of S in the periodic table is an insufficient response.)

Larger atoms make weaker bonds to H than smaller atoms do because of size mismatch, so they are poorer bases. Larger atoms are better nucleophiles because they are solvated more weakly by hydrogen-bonding with MeOH, the solvent in which nucleophilicity is traditionally measured, for the same reason. Their increased polarizability (squishiness) also makes them better nucleophiles.