1) Give the expected products when 3,3-dimethyl-1-butene is treated with each of the following reagents:
   a) Br₂/CH₃OH
   b) Hg(OAc)₂, H₂O, THF, then NaBD₄, OH⁻
   c) H₂O/H₂SO₄
   d) BH₃, THF, then H₂O₂/OH⁻
   e) CH₃COOOH, then H₃O⁺

   Here is the scheme; answers only are given, with some annotations:

   a) Br
   H₃CO
   attack at the weaker C-Br bond, which is the tertiary site.
   b) D
   HO
   Markovnikov orientation; recall the BD₄⁻ replaces the Hg(OAc) group
   c) HO
   carbocationic rearrangement!
   d) OH
   e) OH
   and enantiomer
   f) O

2) Compound A, C₉H₁₆, was found to be optically active. On catalytic reduction over a palladium catalyst, 2 equivalents of hydrogen were absorbed to yield
compound B. Ozonolysis of A gave two compounds. One was identified as acetaldehyde, CH₃CHO; the other compound, C, was an optically active dialdehyde, C₅H₈O₂. By formulating the reactions involved, determine the structures of A, B, and C.

It is often easier to work backwards in these type problems i.e. find C and from that, work to find A, B. We know, from two different data, that A has two degrees of unsaturation, both π-bonds. (Two equivalent of H₂, and the ozonolysis reaction tell us this fact.) The aldehyde group needs to be at the end of the chain, and is the –CHO group, so that uses up two carbons, leaving three. A three-carbon chain (terminating in the –CHO groups) does not allow for optical activity; therefore, we must have a four-carbon chain, with a methyl group on it. Therefore, C must be:

![Structure of C]

We have now accounted for 5 of the nine carbons in A; two acetaldehyde groups would give us both the needed number of carbons, and the correct number of π-bonds. We can now conclude that A is:

![Structure of A](or E/Z isomers)

which makes B:

![Structure of B]

The reactions are:
3) Addition of bromine to compound 1 leads in straightforward fashion to compounds 2 and 3. Write perfect arrow formalisms for those reactions. Less straightforward (but certainly doable) is the formation of compounds 4 and 5. Look carefully at your mechanism for the formation of 2 and 3, and find a route to 4 and 5.

Not much more to say than here it is:
4) Provide syntheses for the following products. You may start from methylenecyclohexane, 1, inorganic reagents of your choice (NO carbons!), and sodium hydride (NaH), diazomethane, tert-butyl alcohol, carbon tetrachloride, chloroform, chlorophyll, clorox, chlordane, chloramphetamines, dimethyl sulfide, trifluoroperacetic acid, and a single frog’s toe. Please pay attention to how you write these answers: “A” means “add chlorox and a frog’s toe all at once,” whereas “B” means “add chlorox, and then, in a second step, add a frog’s toe.”.

A

\[
\begin{array}{c}
\text{X} \quad \text{chlorox} \\
\text{frog’s toe}
\end{array}
\]

B

\[
\begin{array}{c}
\text{X} \quad 1) \text{chlorox} \\
\text{2) frog’s toe}
\end{array}
\]
Well, here are the answers, sort of as a “laundry list” of reagents.

(a) CH₂N₂/hv
(b) trifluoperacetic acid
(c) i) OsO₄, H₂O; ii) NaSO₃, H₃O⁺ (can also use KMnO₄/OH⁻)
(d) Br₂/H₂O (competing nucleophiles)
(e) i) BH₃; ii) H₂O₂, OH⁻
(f) product from (e) + HBr
(g) i) product from (e) + NaH; ii) product from (f)
(h) H₂/Pd (can also use H₂/Rh or H₂/PtO₂)
(i) i) HBr; ii) K O-t-Bu (from t-BuOH + NaH)/t-BuOH (Zeitsev’s Rule) (Can also do:
  i) H₃O⁺/H₂O; ii) stronger H₃O⁺/heat (dehydration reaction; still follows Zeitsev’s Rule))
(j) i) product from (i) + Br₂; ii) K O-t-Bu (from t-BuOH + NaH)/t-BuOH (Can also make
  the glycol, then doubly dehydrate with stronger acid.)
(k) i) O₃; ii) H₂O₂