

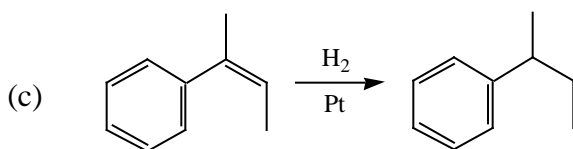
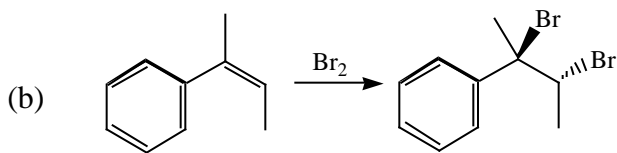
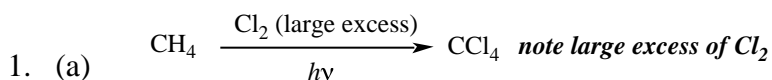
Chem 30A Fall 2002 Exam 3 Solutions Page 1

Statistics: High score = 93 Average = 59.1 Low score = 05

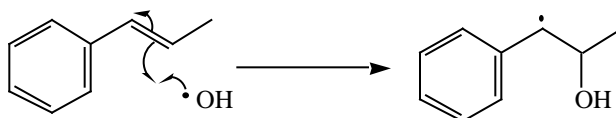
Standard Deviation = irrelevant as it does not control grade distribution in this class.

A note about exam keys: The answers presented here are usually significantly longer than expected from a student taking the exam. An exam key serves not only to reveal what was expected, but to instruct you as well.

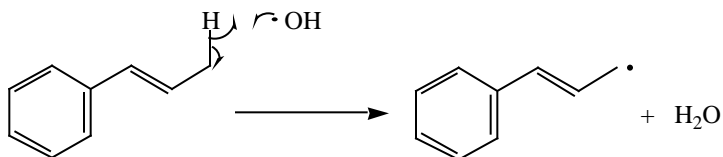
To see the final course grade cutoffs, consult "If Grades Were Assigned Today" at the Chem 30A Home Page.



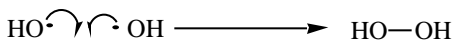
2. Addition to Bond:



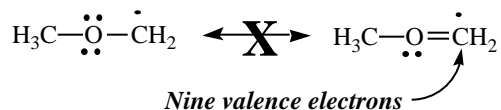
Atom Transfer:

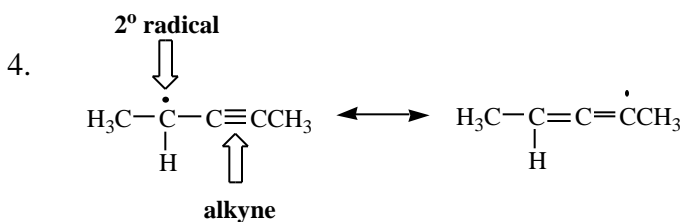


Radical Combination:

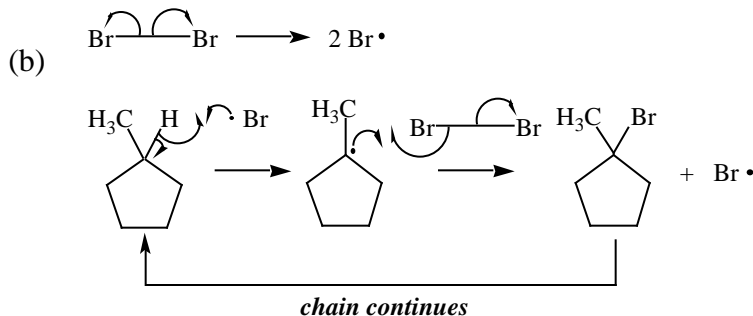


3. This radical **does not** have resonance stabilization, as this would require the carbon to have nine electrons in its valence shell. This impossibility prevents resonance involving a carbon radical and adjacent lone pair of any sort.



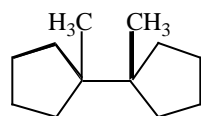


5. (a) The major product of this reaction is **D**.

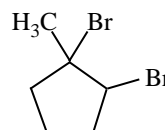


(c) The site of the new C-Br bond is controlled by which radical is formed when Br radical abstracts a hydrogen atom (second mechanism step). In any instance when there is a choice of products, the most stable product has the lowest G^\ddagger and is therefore formed in the greatest amount (i.e., is the major product). In this case the most stable radical is tertiary.

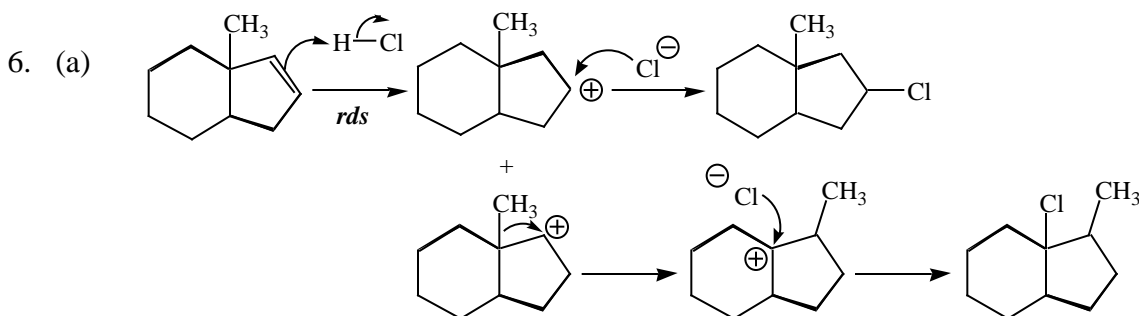
(d) Any reasonable reaction product that is not shown in the question itself is acceptable. Acceptable answers include HBr, and products of radical combination or multiple bromination. Some examples are shown here.



Radical combination product



Multiple bromination product

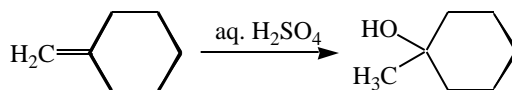


(b) The major products of this reaction are **E** and **F**.

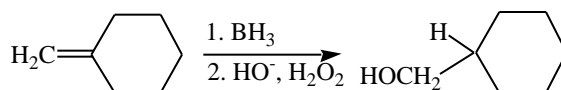
(c) Product **G** is derived from carbocation capture of water. Since not water is present, product **G** cannot be formed at all. Products **E** and **F** are derived from

the same rate-determining step (protonation of the alkene by HCl) so they are formed in approximately equal amounts. Rearrangement to the tertiary carbocation precursor to **F** is much faster than the HCl addition step, so it does not influence the **E** : **F** ratio.

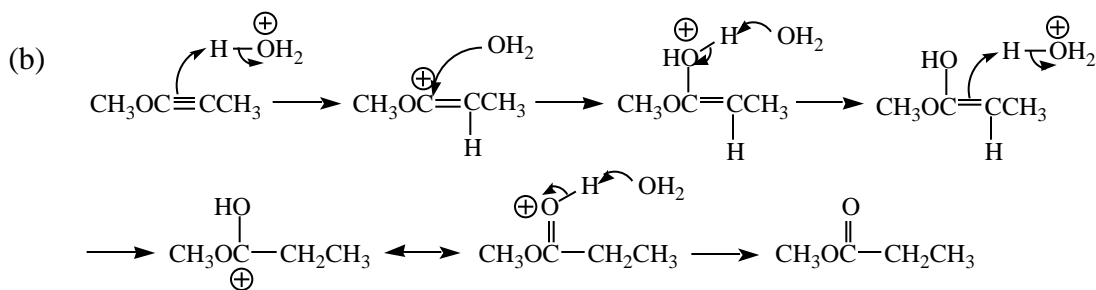
7. Markovnikov addition: The proton end of the electrophile becomes attached to the alkene carbon bearing the greatest number of hydrogens. (“Them that has, gets.”)



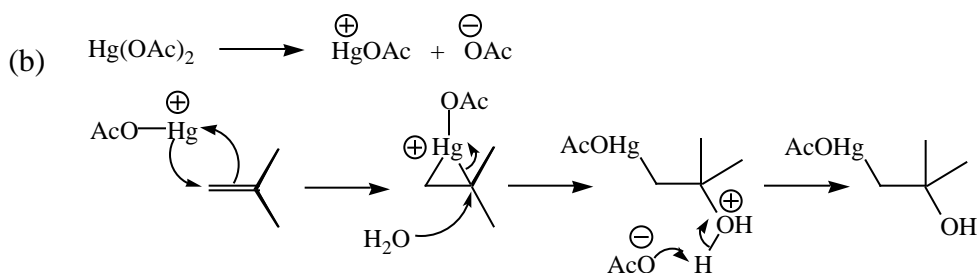
Anti-Markovnikov addition: The proton end of the electrophile becomes attached to the alkene carbon bearing the least number of hydrogens.



8. (a) The major product of this reaction is **H**.



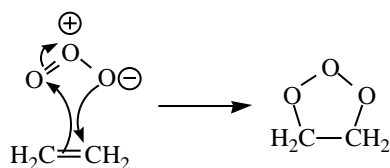
9. (a) The major product of this reaction is **J**.



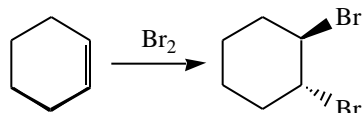
10. Reason #1: NH_4^+ ($\text{p}K_a$ 10) is a much weaker acid than H_3O^+ ($\text{p}K_a$ -1.78).

Reason #2: Nitrogen is less electronegative than oxygen so the hydrogens of NH_4^+ have less + charge than the hydrogens of H_3O^+ . This makes NH_4^+ a weaker electrophile.

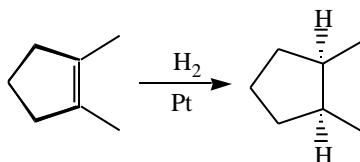
11. (a) Cycloaddition reaction: An addition reaction that results in a new ring. Example: First mechanism step of alkene ozonolysis reaction.



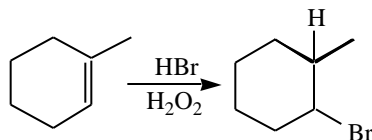
- (b) Anti addition reaction: Addition reaction in which the fragments of the molecule added become bonded to opposite faces of the bond. Example: Addition of Br₂ to cyclohexene.



- (c) Addition to a C-C bond that does not involve an electrophile: The only C-C bond addition reaction that we have studied that does not involve a distinct electrophile is catalytic hydrogenation.



- (d) Peroxide effect: Addition of HBr to a C-C bond in the presence of a peroxide such as H₂O₂ proceeds via a radical mechanism to give the anti-Markovnikov product.



12.

