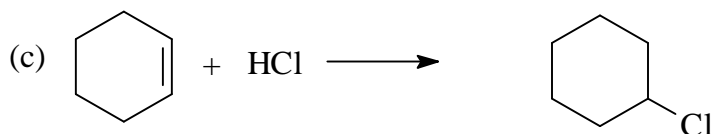
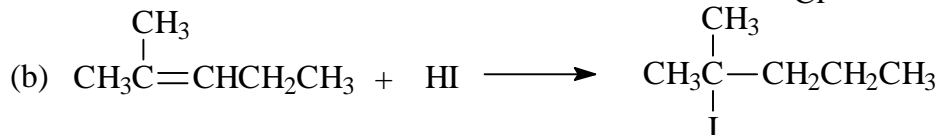
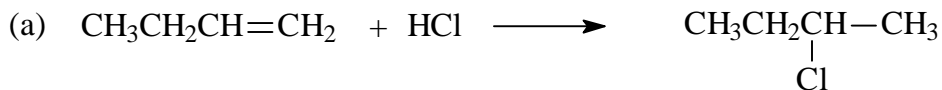


Chapter 4

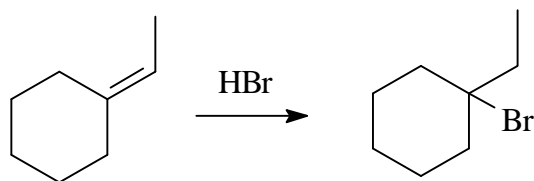
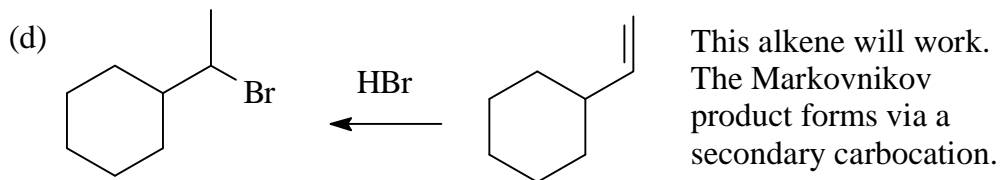
1. Predict the products of the following reactions.



In (a) and (b) the Markovnikov product is the major product and is the one shown. In (a) this product forms via the secondary carbocation which is more stable than the alternative primary one. In (b) the tertiary carbocation is formed faster than the secondary, leading to the product shown. In (c) only one product is possible.

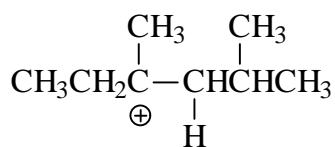
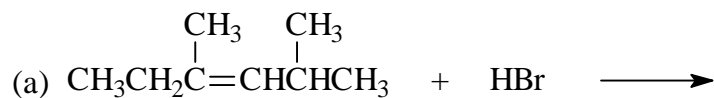
2. What alkenes would you start with to prepare the following alkyl halides?

(a) bromocyclopentane. Add HBr to cyclopentene.

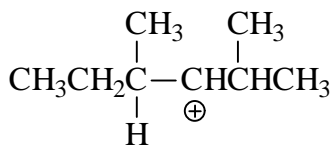


This alkene is not satisfactory. The major product is the Markovnikov product formed via the more stable tertiary carbocation.

3. Show the structures of the carbocation intermediates you would expect in the following reactions.

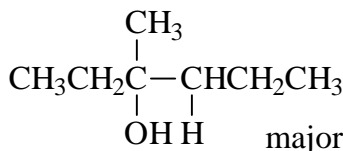
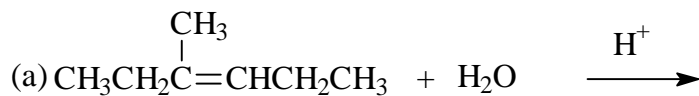


tertiary - major



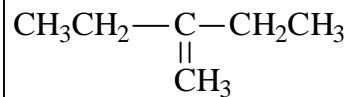
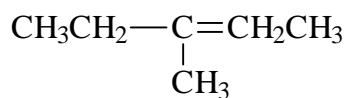
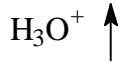
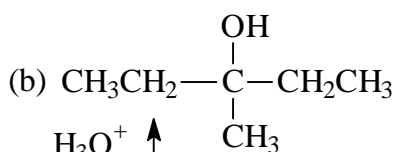
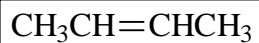
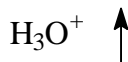
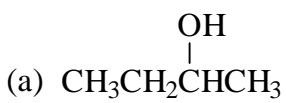
secondary - very little formed

4. What product would you expect to obtain from addition of water to the following alkenes?



major product

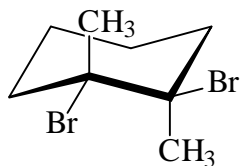
5. What alkenes might the following alcohols be made from?



In each case I have enclosed the better choice in a box, but either compound would be suitable.

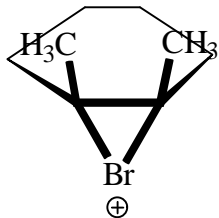
Why is the boxed choice better?

6. What product would you expect to obtain from addition of Br_2 to 1,2-dimethylcyclohexene? Show the stereochemistry of the product.

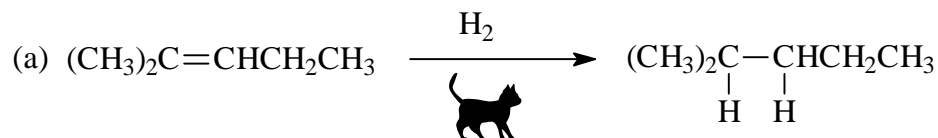


The product is *trans*-1,2-dibromo-1,2-dimethylcyclohexane, resulting from anti addition of the bromines. The conformation with the bromines equatorial, is shown. What is the alternative conformation?

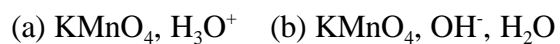
7. Show the structure of the intermediate bromonium ion formed in Problem 4.6.



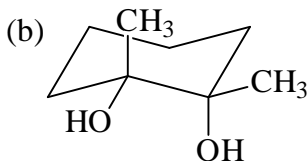
8. What product would you expect to obtain from catalytic hydrogenation of the following alkenes?



9. Predict the product of the reaction of 1,2-dimethylcyclohexene with the following.



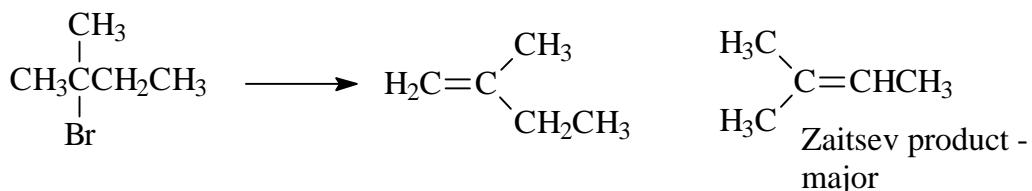
Under acidic conditions (a) the double bond will be completely cleaved. The result in this case will be a diketone. Under basic conditions (b) an OH group will become attached to each of the carbons formerly joined by the double bond. This is a syn addition.



11. Show the structure of Teflon by drawing several repeating units. The monomer unit is tetrafluoroethylene, $F_2C=CF_2$.

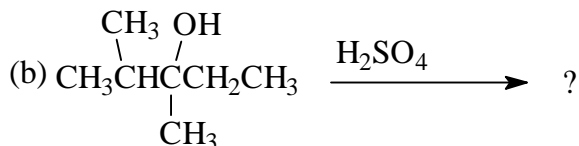
The monomer alkene units add together to produce the polymer, in this case $-CF_2-CF_2-CF_2-$.

12. What products would you expect from the reaction of 2-bromo-2-methylbutane with KOH in ethanol? Which will be major?

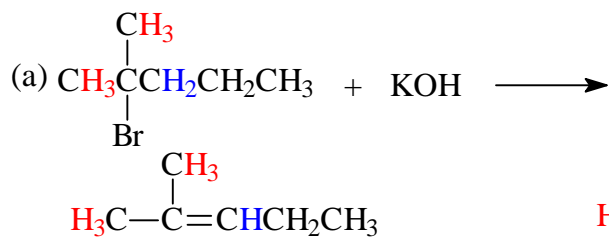


In dehydrohalogenations the more highly substituted (with alkyl groups) alkene (Zaitsev's rule) is preferred. But, usually, this preference is not very strong, so a mixture is formed. This is in contrast to the Markovnikov rule where preference usually is pretty strong.

14. Predict the products you would expect from the following reactions. Indicate the major product in each case.

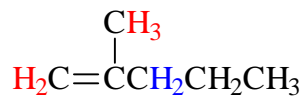


Answers:

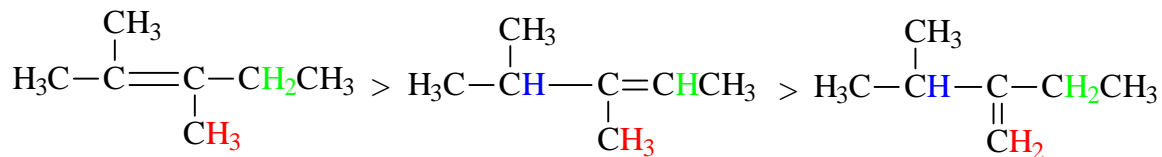
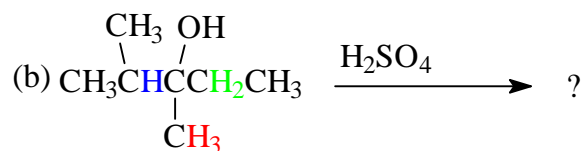


Removal of either of the two blue hydrogens along with the Br leads to this product.

This product is likely to predominate because it is the more highly substituted alkene (Zaitsev's rule).

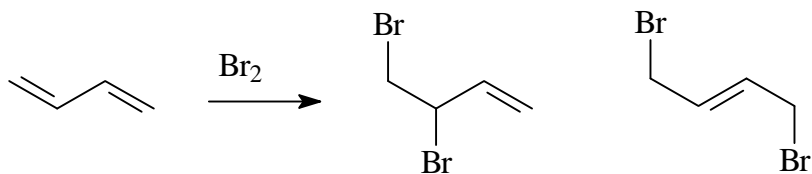


Removal of any of the six red hydrogens along with the Br leads to this product.



The more highly substituted the alkene, the faster it forms. This is another example of Zaitsev's rule.

16. 1,3-Butadiene reacts with Br_2 to yield a mixture of 1,2- and 1,4-addition products. Show the structure of each.

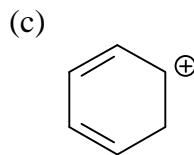
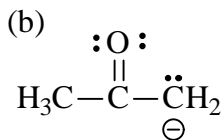
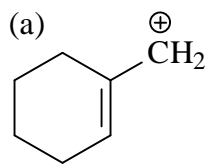


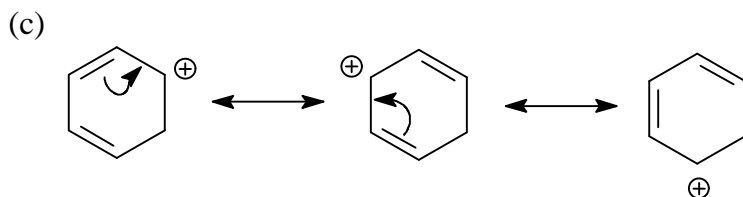
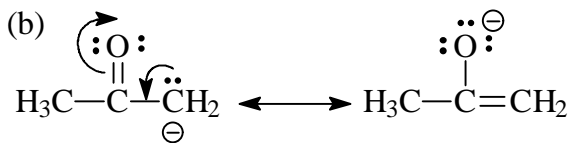
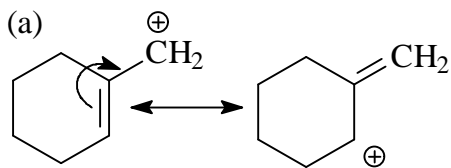
1,2-addition

1,4-addition

Note the position of the double bond.

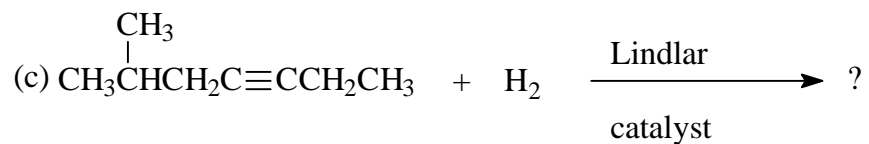
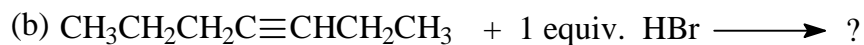
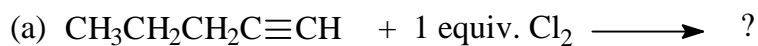
19. Draw as many resonance structures as you can for the following species.

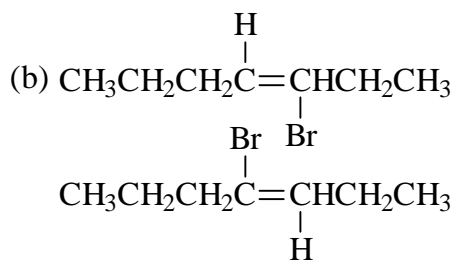
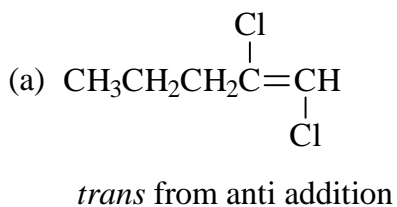




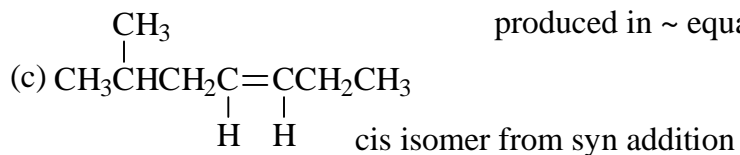
When drawing resonance structures it is sometimes handy to use the curved arrows as “electron bookkeeping devices.” For beginners it would probably be wise to at least draw in the hydrogen atoms on the stick structures so the atomic valencies will be obvious.

21. What products would you expect from the following reactions?

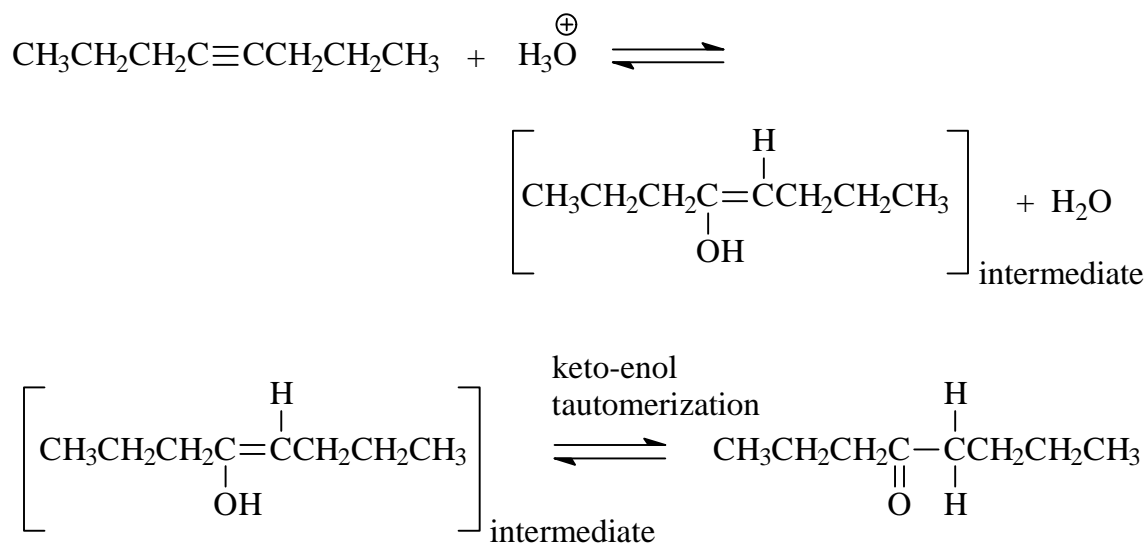




Both *trans* from anti addition;
 produced in ~ equal amounts.

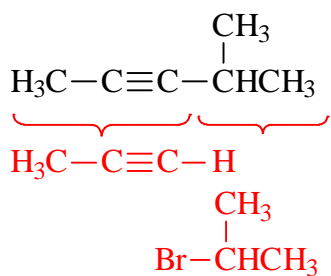
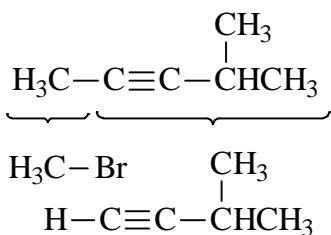
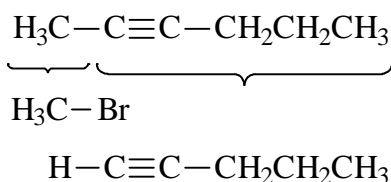
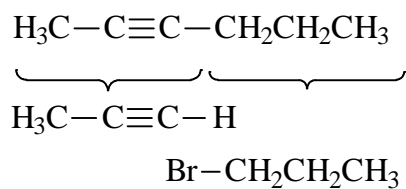
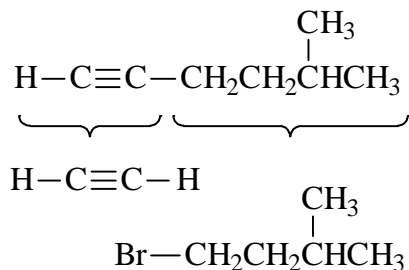


22. What product would you obtain by hydration of 4-octyne?



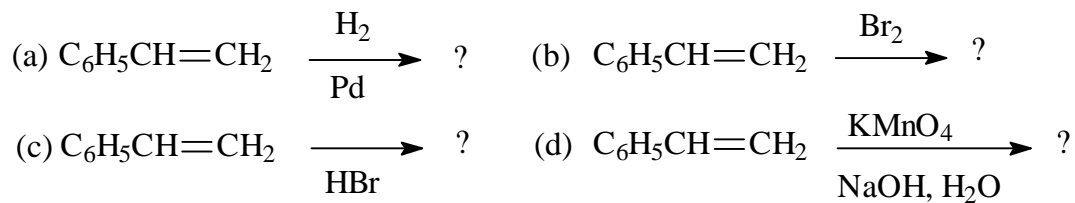
24. Show the alkyne and alkyl halide from which the following products can be obtained. Where two routes look feasible, list both.

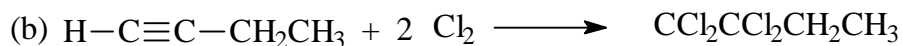
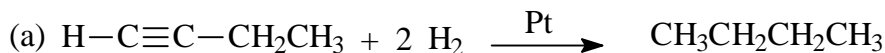
(a) 5-methyl-1-hexyne, (b) 2-hexyne, (c) 4-methyl-2-pentyne



This will not work. The alkyl halide must be primary (or methyl). Secondary and tertiary alkyl halides undergo elimination under basic conditions to give alkenes rather than the desired product.

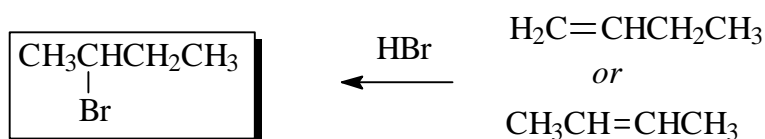
33. Predict the products of the following reactions. Indicate regioselectivity where relevant. (The aromatic ring is inert to all the indicated reagents.)



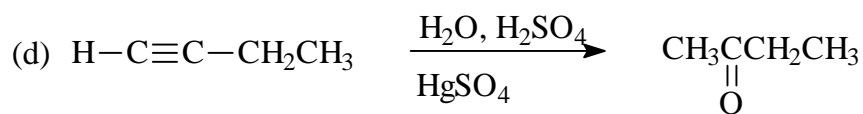
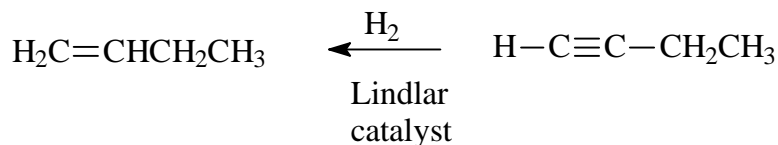


- (c) As synthesis problems become more involved, it is often useful to focus on the molecule you are trying to make and think of any ways you can make it. Then, think about how you can make the compound you used to make the target molecule, *etc.*

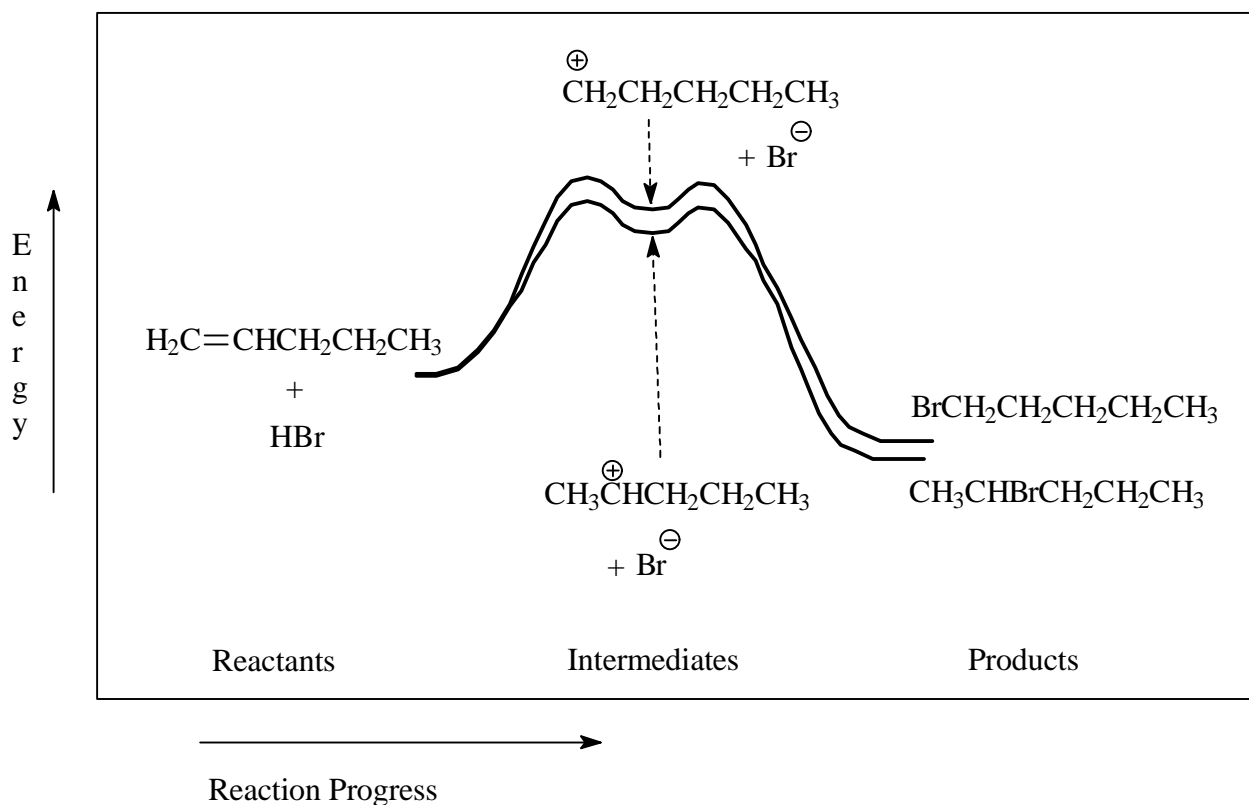
In other words, work backwards.



This is a method we know for making alkyl halides. Now, we need to make an alkene. This can be done by dehydration of an alcohol, dehydrohalogenation of an alkyl halide, or Lindlar hydrogenation of an alkyne. Dehydrohalogenation is just the reverse of what we have just done, so that doesn't seem to be very productive. On the other hand, Lindlar hydrogenation sounds good since we are supposed to start with 1-butyne.



53. Draw a reaction energy diagram for the addition of HBr to 1-pentene. Let one curve on your diagram show the formation of 1-bromopentane product and another curve on the same diagram show the formation of 2-bromopentane product. Label the positions for all reactants, intermediates, and products.



The important thing here are that the secondary carbocation is more stable (lower in energy) than the primary carbocation. Also, it is noteworthy that the E_{act} for formation of the secondary carbocation is smaller than for the primary. I have shown an energy difference in the products, but I don't know that this is the case. It doesn't really matter. The more stable secondary carbocation forms faster than the primary carbocation. Consequently, more secondary carbocation is produced. Secondary carbocation forms 2-bromopentane; hence more of this is produced.