CHEM116 Fall 2001 Exam #3
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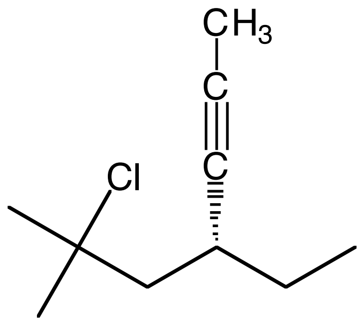
ANSWER KEY

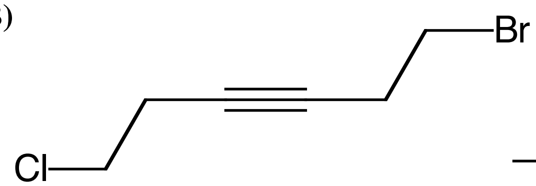
1) Provide an unambiguous name for each of the following molecules. (12 points)

A)



(*R*)-6-Chloro-4-ethyl-6-methyl-2-heptyne

B)



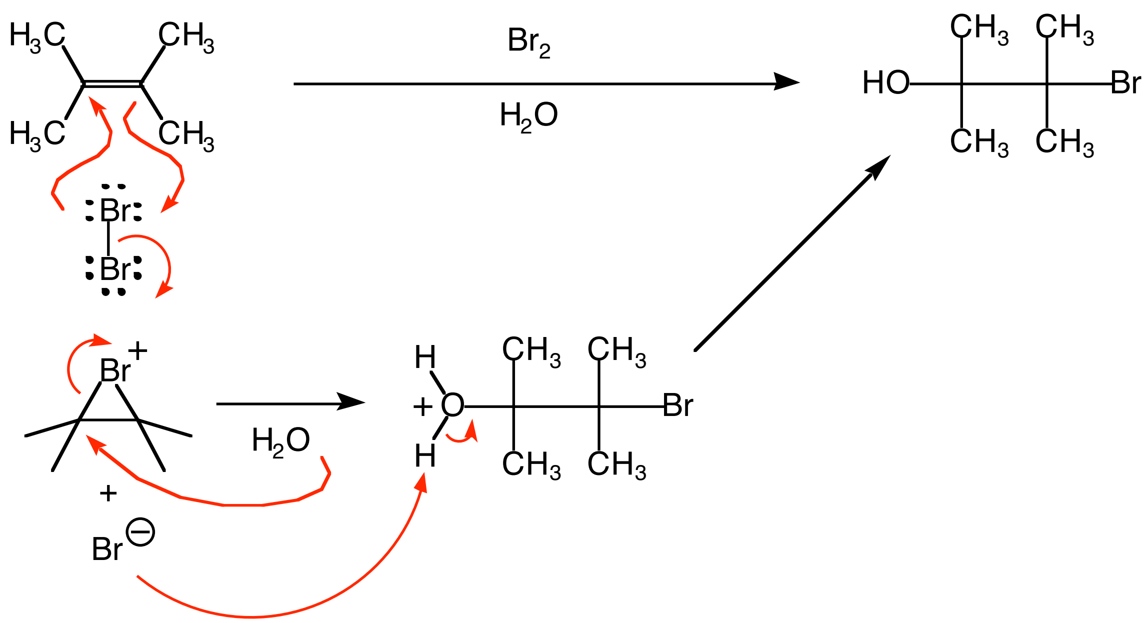
1-Bromo-6-chloro-3-hexyne

2) For many years, chemists have attempted to synthesize the two molecules shown below. Molecule A was easy to synthesize, but to this date, molecule **B** has been impossible to synthesize. Explain why this is an unusual result. Then using pictures *and* words, explain why **B** is so difficult to make, while **A** is a piece-of-cake. (10 points)

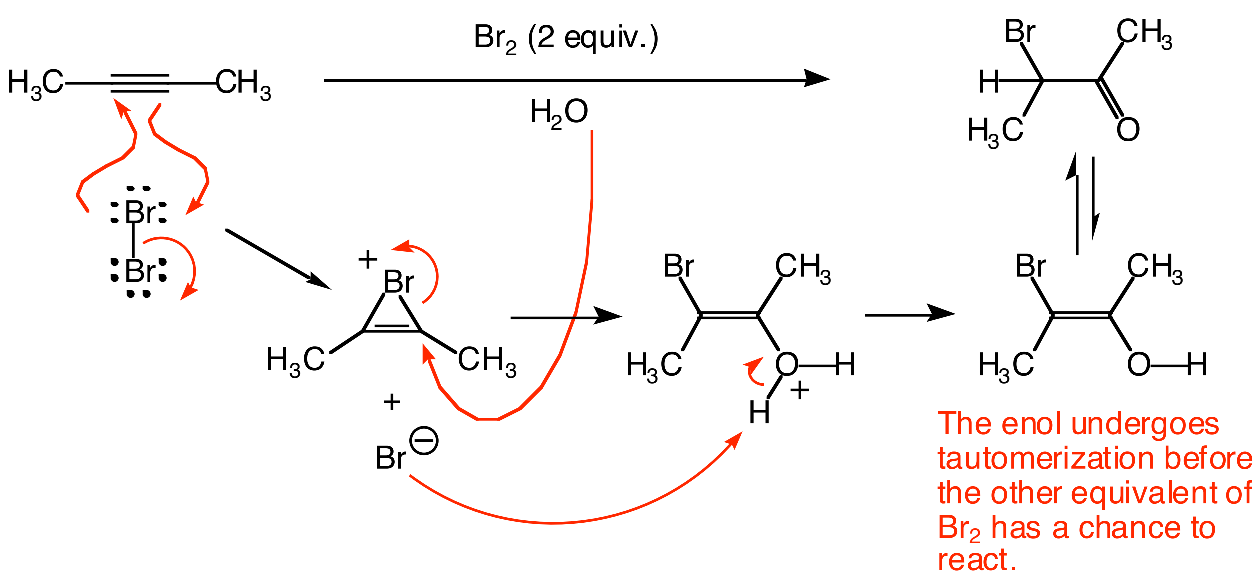
This is an unusual result because one would expect A to have more angle strain and thus make the molecule much less stable than B. However, both A and B possess a resonance structure in which an empty p orbital becomes part of the ring. In A, this resonance structure is aromatic (planar, cyclic, conjugated, 2π electrons) and thus makes the molecule very stable. In B, the resonance structure is antiaromatic (planar, cyclic, conjugated, 4π electrons) , making the molecule very unstable and consequently, very difficult to synthesize.

3) We've seen that many of the reagents that react with alkenes also react with alkynes. However, some alkene reactions are not equally applicable to alkynes. Two reactions are shown below. Provide a mechanism for reaction **A**. Then provide a mechanism for reaction **B** that explains why the alkyne *does not add* two Br's and two OH's. Of course, you will need to predict the product that *does* form in reaction **B**. (22 points)

Reaction A

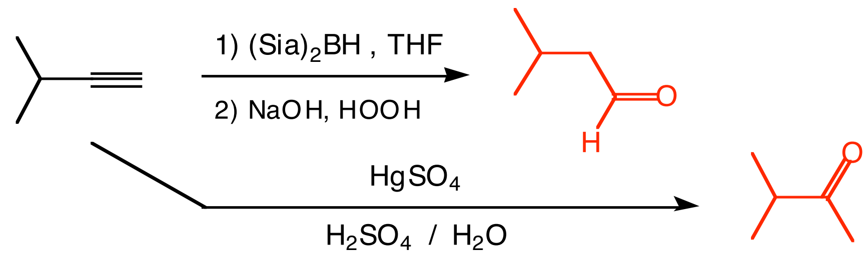


Reaction B

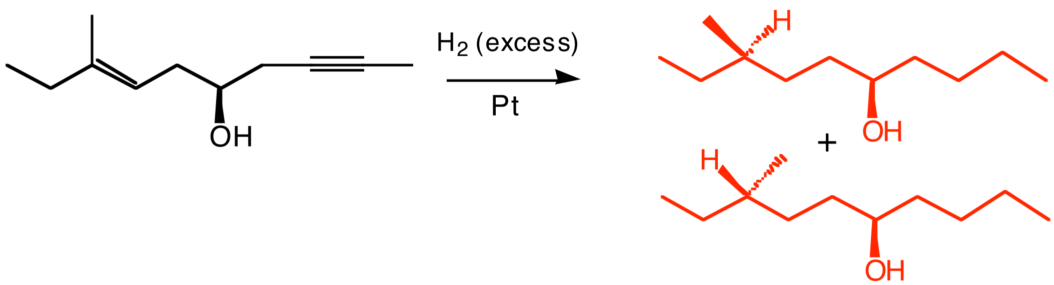


4) Predict the major organic product of each of the following reactions. (26 points)

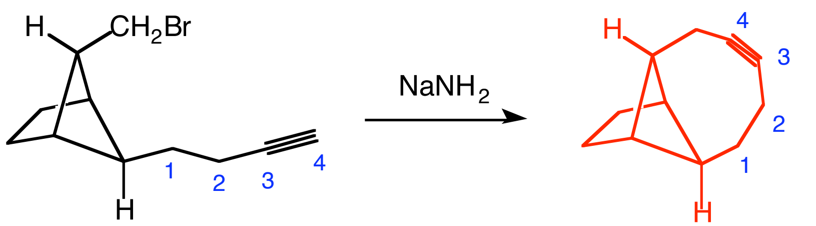
A)



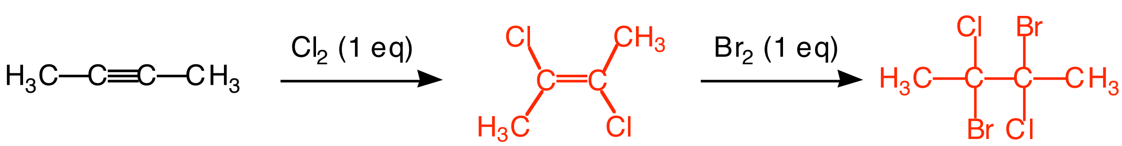
B)



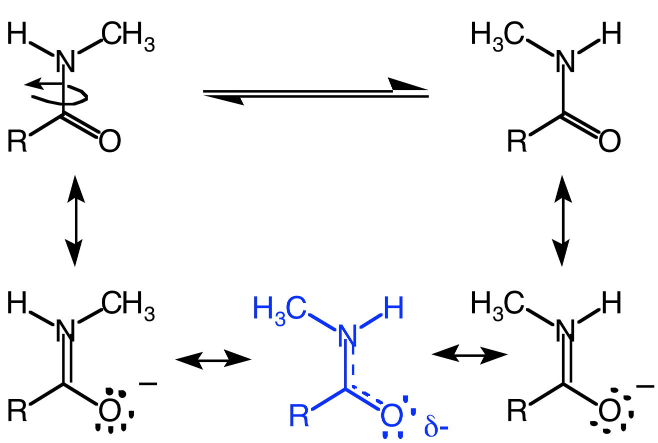
C)



D)



5) In her research, Dr. Hatcher-Skeers works with compounds known as amides. Her research group has found that at lower temperatures, amides like the one shown below actually appear to be two different molecules, while at higher temperatures only one molecule is visible. Use pictures *and* words to explain this phenomenon. (8 points)

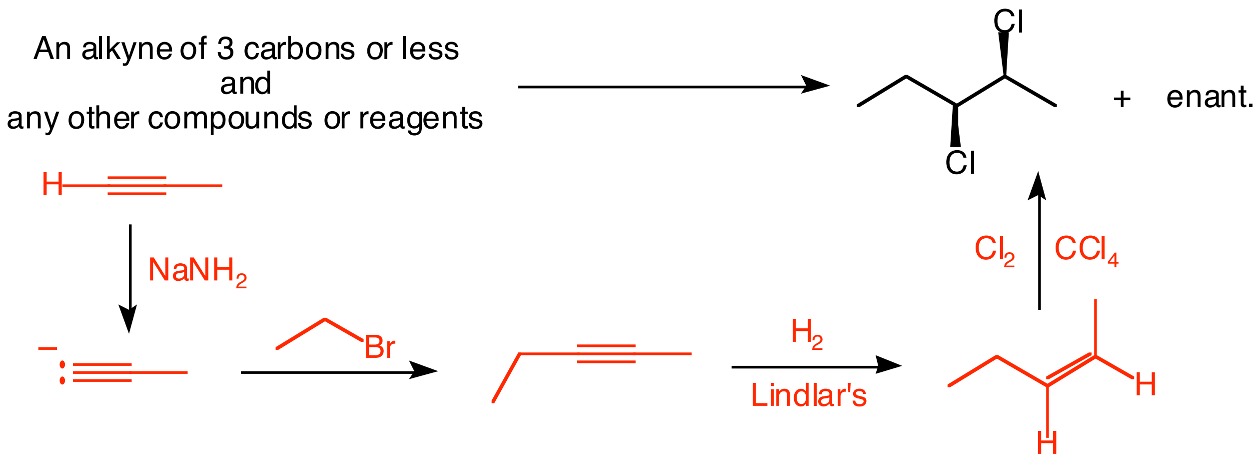


The C-N bond, as a single bond, exhibits free rotation. Therefore, the molecule exists in two major conformations as shown.

Each conformation has a resonance structure that is a diastereomer of the other. We know that the molecule will exist as a hybrid where the C-N bond is not quite a single bond and not quite a double bond. Because it has some characteristics of a double bond, it will exhibit limited rotation. At low temps, there is not enough energy for bond rotation to occur. So the molecule will be stuck in its two conformations and look like two different molecules. At higher temperatures, there is enough energy available to cause free rotation of the bond.

ANSWER KEY

6) Provide a synthesis for the following transformation. Show the products of each step for full credit. (10 points)



7) Molecule **A** is an optically active compound with a mol. formula of C_8H_{12}. It reacts with an excess of HBr to yield **B**, an optically active compound with a formula of $C_8H_{14}Br_2$. When **A** is subjected to cat. hydrogenation using an excess of H_2 gas, it yields **C**, an optically inactive compound (MF = C_8H_{16}). Both dissolving metal reduction and Lindlar's hydrogenation of **A** yield the same optically active molecule, **D** (MF = C_8H_{14}). Provide structures for **A-D** below. (12 points)

One of several possibilities...