

Chemistry 230-002 Final Examination

Dr. Grossman's Section

December 15, 2005

Name (please PRINT LEGIBLY) _____
(last) (first)

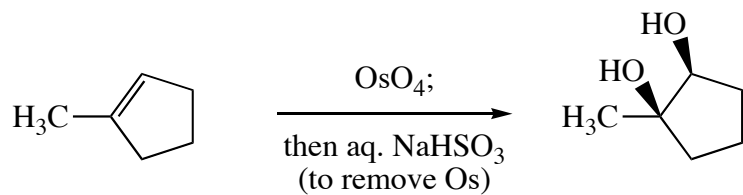
<u>Problem</u>	<u>Score</u>	
1. (a-h)	_____	/32
2. (a-b)	_____	/32
3. (a-b)	_____	/32
4. (a-f)	_____	/26
5. (a-d)	_____	/16
6. (a-d)	_____	/16
<u>Total</u>	_____	/154

Please observe the following.

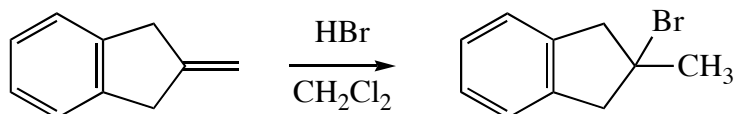
- 1) Write LARGE and LEGIBLY.
- 2) Read each question carefully before answering. Many points are never awarded on every exam because students do not read the instructions.
- 3) Explanations must be clear, coherent, and unambiguous to receive credit.
- 4) Your percentage score will be calculated on the basis of 150 points, not 154 points. In other words, there are four points of extra credit on this exam.

1. (4 pts. each, 32 pts. total) Draw the *major* product of each of the following reactions. Be sure to indicate the stereochemistry of the product, if appropriate.

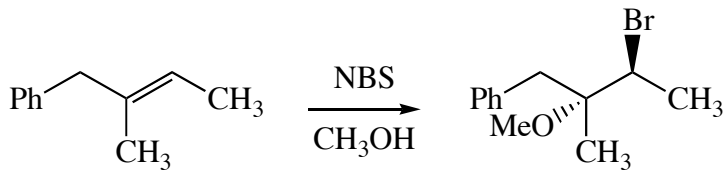
(a)



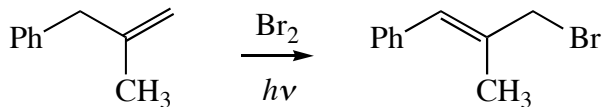
(b)



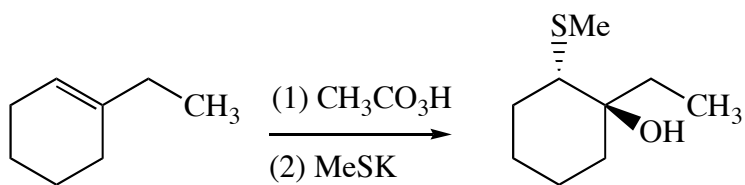
(c)



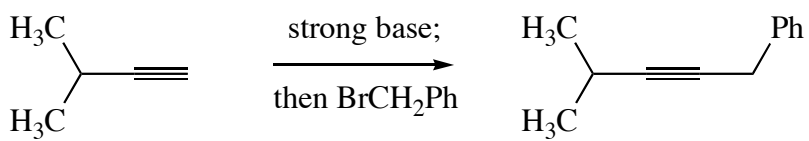
(d)



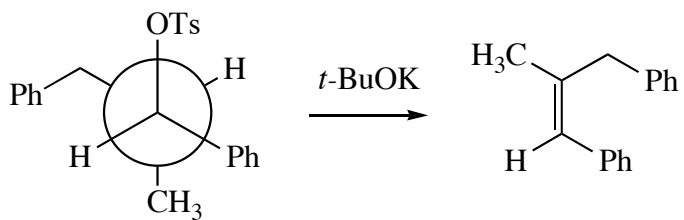
(e)



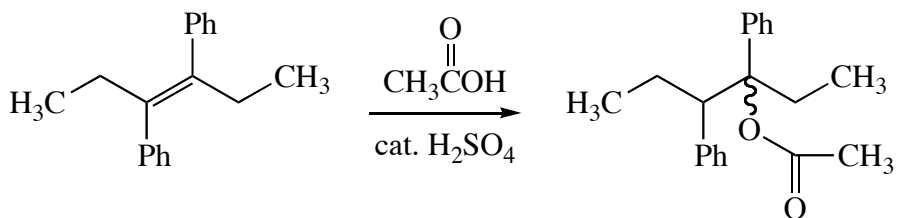
(f)



(g)

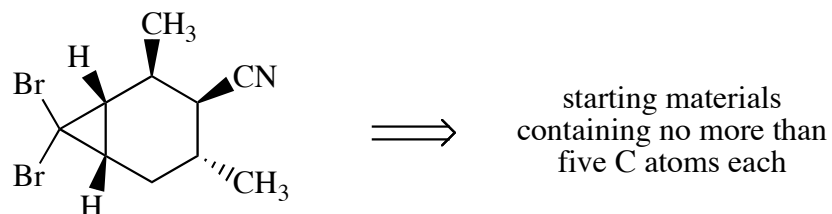


(h)

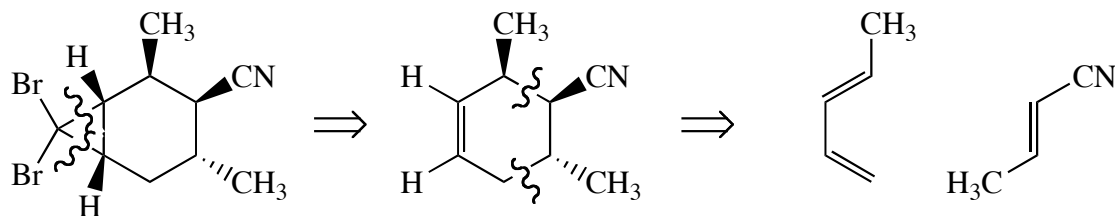


2. (32 pts. total) Design syntheses of each of the following compounds from the indicated starting materials. Show all reagents required for each transformation. You are advised to conduct a retrosynthetic analysis before working in the forward direction. Each synthesis will require more than one step.

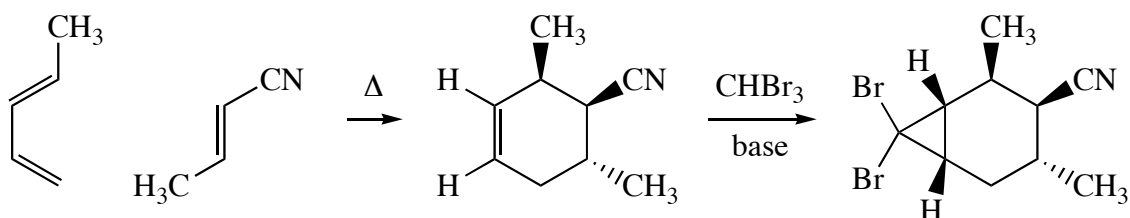
(a) (16 pts.)



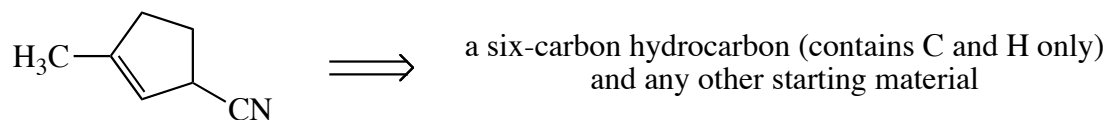
Retro:



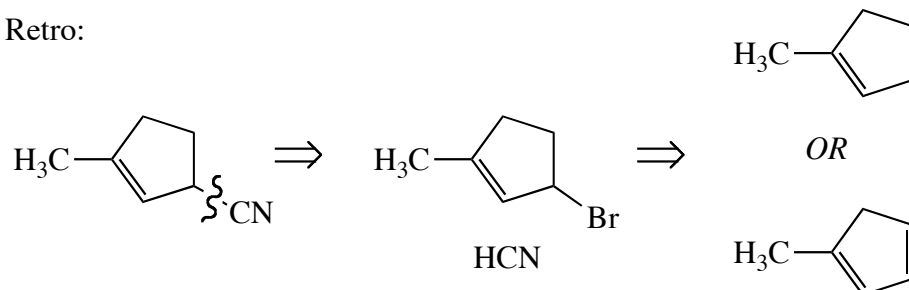
Forward:



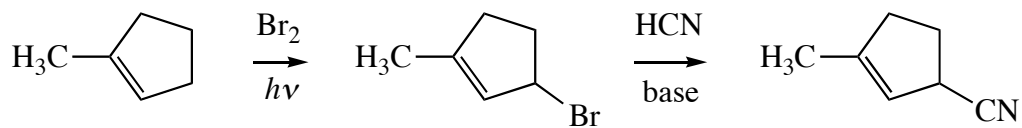
(b) (16 pts.)



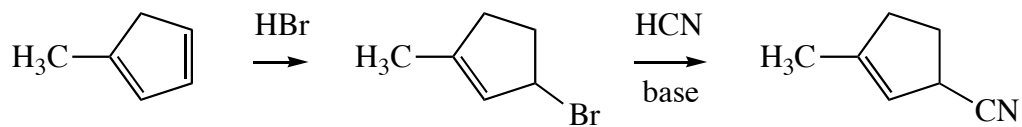
Retro:



Forward:



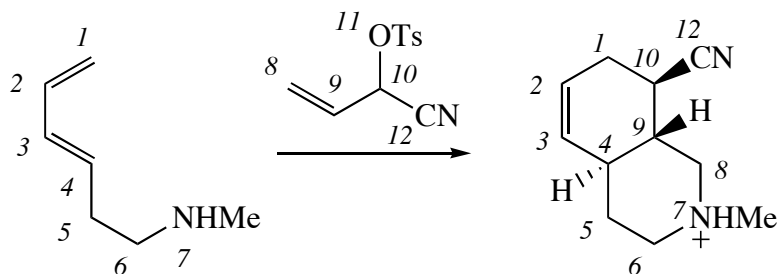
OR



3. (32 pts. total) Draw reasonable mechanisms for each of the following reactions. Use the curved arrow convention to show the movement of electrons. If the reaction proceeds by a free-radical mechanism, *draw* and *clearly label* the initiation and propagation steps; you do not need to draw termination steps.

Remember to obey Grossman's Rule!

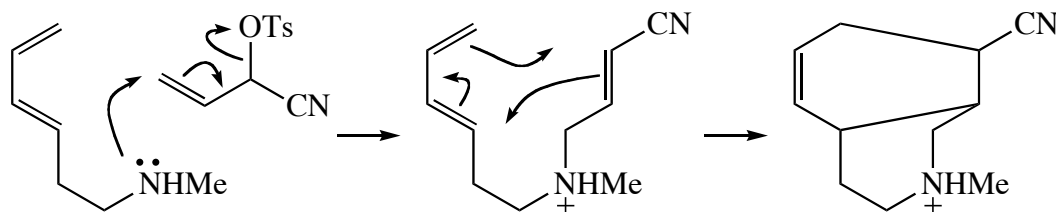
(a) (10 pts.)



Make: C1–C10, C4–C9, N7–C8.

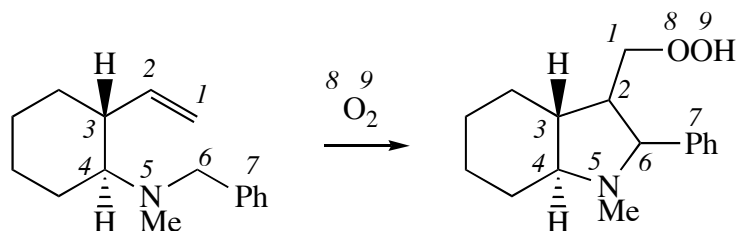
Break: C10–O11.

N7 is a nucleophile, and C8 is an electrophile (because C10 is one) so start off making N7–C8.



Remember to obey Grossman's Rule!

(b) (22 pts.)

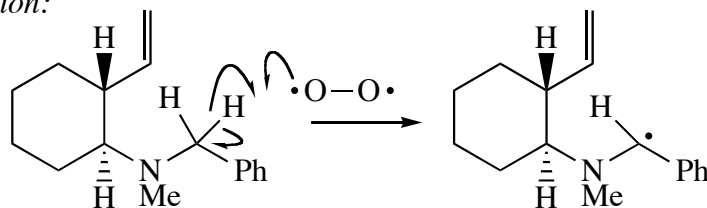


Make: C1–O8, C2–C6, O9–H.

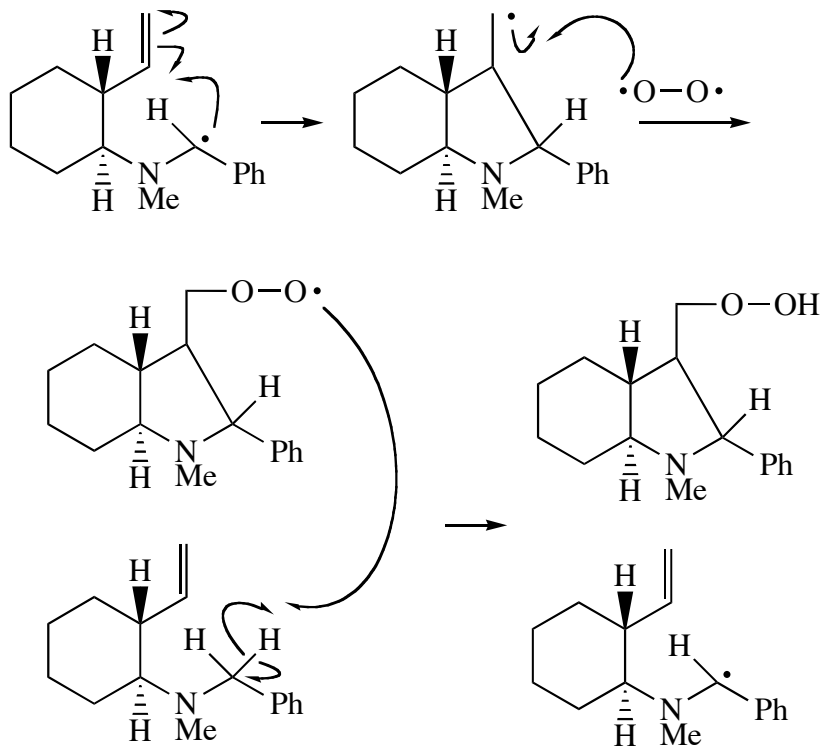
Break: C6–H.

The presence of O_2 is a clue that this is a free-radical reaction. Initiation involves O_2 abstracting an H. Which H? The one that needs to be abstracted.

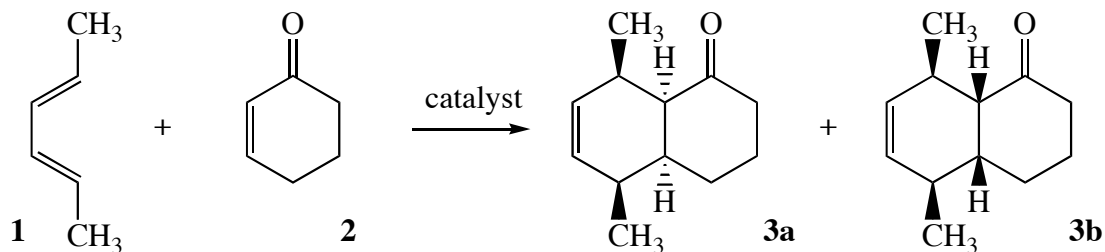
Initiation:



Propagation:



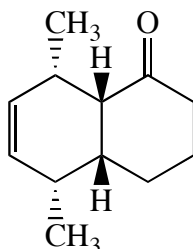
4. (26 pts. total) Consider the following Diels–Alder reaction of **1** and **2** to give **3a** and **3b**.



(a) (4 pts.) Describe the relationship of compounds **3a** and **3b** in two words or fewer and as specifically as possible. (You will lose one point if you misspell.)

configurational diastereomer

(b) (4 pts.) Draw the enantiomer of **3a**. (The answer may or may not be **3b**.)



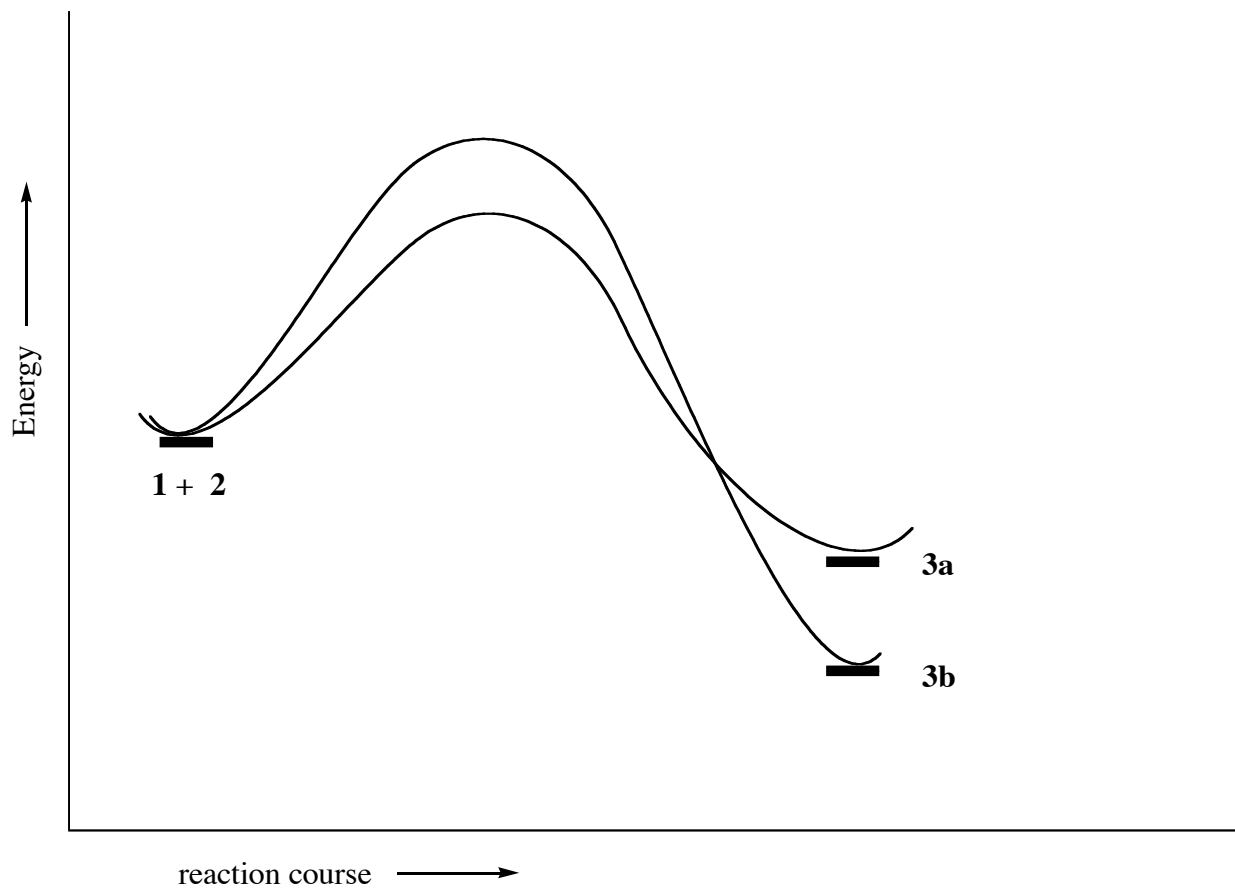
(c) (4 pts.) Is **3a** higher in energy than **3b**, lower in energy than **3b**, about the same energy as **3b**, or is there no way to tell? Explain your answer *briefly* and *coherently*.

3a is higher in energy because the two Me groups are cis to the right-hand ring. In **3b**, the two Me groups are cis to the H atoms at the ring fusion.

(d) (4 pts.) In the reaction above, is more **3a** obtained, more **3b**, about the same amounts, or is there no way to tell? Explain your answer *briefly* and *coherently*.

More **3a** is obtained because the carbonyl group prefers to be endo, and the out–endo→cis mnemonic device tells you that the Me groups will be cis to the carbonyl in the major product.

(e) (6 pts.) Using the information provided and your answers to (c) and (d), draw a reaction coordinate diagram that shows the proper relative energies of starting materials, transition states, and products in this reaction. *Clearly* label which product is **3a** and which one is **3b**. (I began the graph for you. One of the curved lines is the beginning of the coordinate leading to **3a**, and the other is the beginning of the coordinate leading to **3b**.)

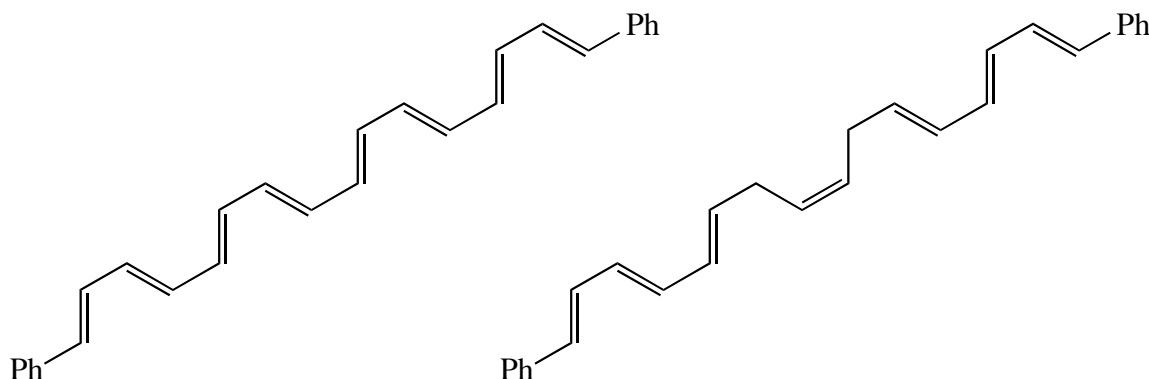


(f) (4 pts., extra credit) How could you modify the reaction above to make **3a** or **3b** in enantiomerically pure form?

Use an enantiomerically pure catalyst.

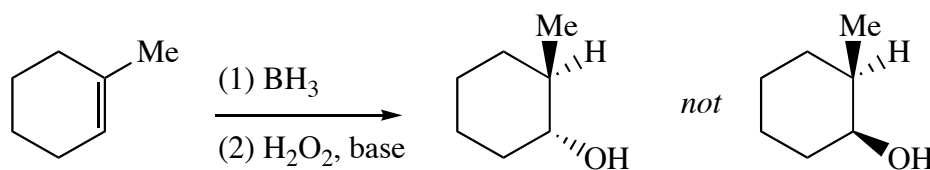
5. (4 pts. each, 16 pts. total) Explain each of the following observations in no more than one or two short, easily understood sentences.

(a) The compound on the left is colored, but the compound on the right is colorless.



The compound on the left is more highly conjugated, i.e., has more π bonds in a row than the one on the right. That means that the HOMO–LUMO gap of the compound on the left is smaller, which means it absorbs lower-energy light, which makes it colored. The compound on the right absorbs only UV light.

(b) Hydroboration–oxidation of an alkene gives only the product of syn addition.

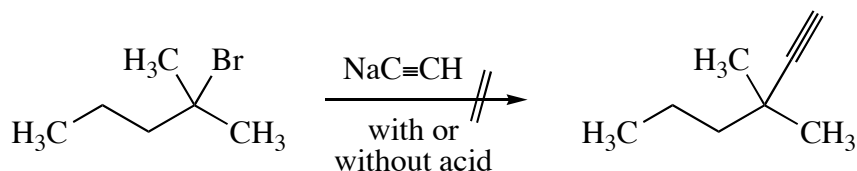


Because the B–H bond adds in concerted fashion across the π bond, and the C–B bond is converted to a C–O bond with retention of configuration about C.

- (c) The reaction of CH_3CH_2^- with H^+ to give CH_3CH_3 is much stronger (more rapid, more exothermic) than the reaction of $\text{HC}\equiv\text{C}^-$ with H^+ to give $\text{HC}\equiv\text{CH}$.

Because the lone pair in $\text{HC}\equiv\text{C}^-$ is in a lower-energy sp orbital, and the lone pair in CH_3CH_2^- is in a higher-energy sp^3 orbital. The higher the energy of the lone pair, the more reactive the compound is.

- (d) The reaction below fails regardless of whether or not acid is added. (Explain both cases.)

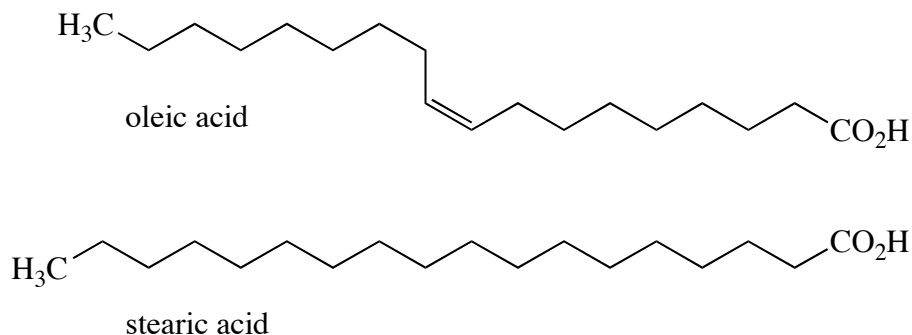


Under basic conditions, the 3° halide does not like to undergo substitution reactions; elimination will occur instead.

Under acidic conditions, the nucleophile will be protonated, so it will no longer be a nucleophile.

6. (4 pts. each, 16 pts. total) Organic chemistry is involved in some important environmental and biological processes.

(a) One reason the food industry likes to use unhealthy saturated fats in their products is that saturated fats do not spoil as quickly as unsaturated fats. Spoilage is often caused by reaction with O_2 . Explain why unsaturated fats such as oleic acid are quicker to spoil than saturated fats such as stearic acid.

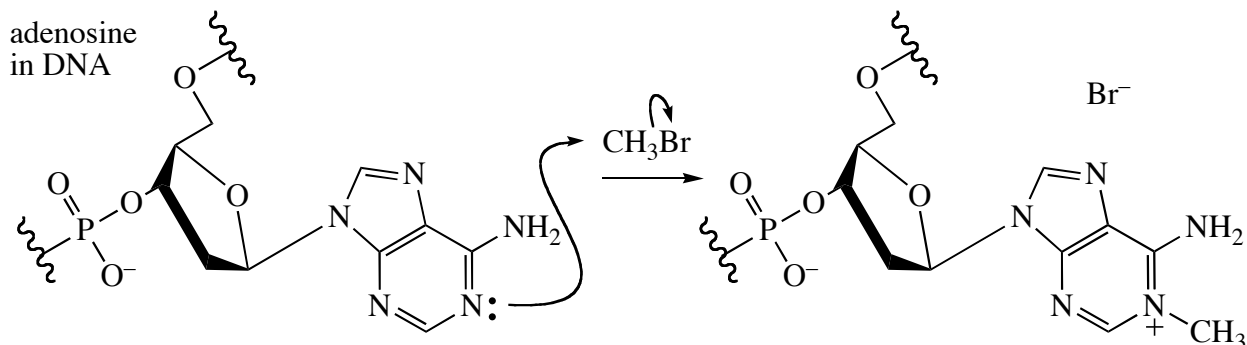


It's easier for O_2 to remove an H atom adjacent to the π bond in oleic acid than it is for it to remove an H atom from stearic acid.

(b) A pile of oily rags in a garage may "spontaneously" catch on fire. A fire is simply a rapid, exothermic reaction of a compound with O_2 . Explain how a slow, slightly exothermic autoxidation reaction can eventually become a fire in a pile of oily rags. (Assume the oil consists of a mixture of alkanes with 10–20 C atoms.)

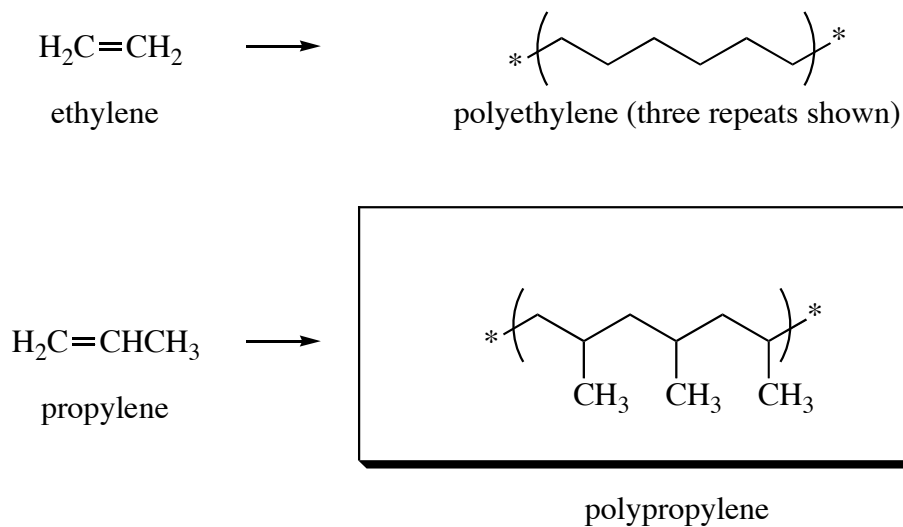
The initial autoxidation reaction of the oil with O_2 releases heat. The heat causes the autoxidation reaction to accelerate, which releases more heat, which accelerates autoxidation even more, which releases even more heat. Eventually a fire breaks out.

(c) Methyl bromide is an agriculturally important fungicide and pesticide, but it is also a potent ozone depleter and a dangerous toxin. One of its mechanisms of toxicity begins with it reacting with DNA. Draw the product of a reaction that methyl bromide can undergo with a DNA base such as adenosine (below). Use curved arrows to show the movement of electrons in the reaction.



(You can use any N or even the O⁻ as the nucleophile.)

(d) The polymerization of ethylene by a free-radical reaction is a hugely important reaction. By contrast, the polymerization of propylene (CH₂=CHCH₃) by a free-radical reaction is much less widely used because polypropylene is obtained as a nasty mixture of diastereomers. Draw polypropylene, showing at least three repeats (polyethylene is shown with three repeats), and show or explain how this three-repeat unit can exist as a mixture of diastereomers.



The three methyl groups can be up, up, up, or up, up, down, or up, down, up, or