Chemistry 210
"Organic Chemistry I"
Winter Semester 2004
Dr. Rainer Glaser

Examination #3
"Chemistry of Unsaturated Hydrocarbons. Elimination and Addition Chemistry."

Posted: Monday, April 19, 2004.
Collect: Wednesday, April 21, 2004, after lecture.

Name:

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Question 1. The Right Chemistry: Ripening Fruit (24 points)

Source: **http://www.bizjournals.com/charlotte/stories/1997/06/02/focus1.html**

The right chemistry - **Local chemical industry's 86 employers roll with the punches**

Edward Martin

On a recent Wednesday morning at the Food Lion supermarket on Eastway Drive, clerks stacked rows of polished tomatoes as shoppers scanned weekly specials and steered carts down the aisles. In west Charlotte, in an industrial area off Pressley Road, Karen Ann Christenbery, her father, Robert Wilson, and their employees were lending a hand.

After beginning as Midwestern grain, the ethanol their firm processes is shipped to Charlotte in 8,000-gallon tankers and packaged into cases of quart or gallon jugs.

From there, it's shipped to produce distributors and grocers like Food Lion, which, a few days before, had fed the liquid through a catalytic generator that heats it into ethylene gas. Exposed tomatoes, bananas, avocados and other produce responds on cue.

"It jump-starts ripening," says Christenbery, vice president of American Ripener Co. Inc. "That's how supermarkets can have produce that's ripe exactly on sale days."

American Ripener in many ways characterizes Charlotte's chemical industry. …

(a) Give the overall reaction of the chemistry used in the catalytic generators employed for fruit ripening. (4 points)

Green Banana Chemistry Experiment

[1] Obtain two hands (bunches) of **green bananas** that have not had ethylene applied to them.
[2] Also obtain several apples.
[3] Place 1 - 2 apples in a sealed container with a hand of bananas. Place the other hand of bananas in a separate sealed container WITHOUT apples.
[4] Place both containers in an area that is 60 - 72°F.
[5] Do not open the containers for 24 hours. After 24 hours and every 24 hours thereafter, remove the lids of the containers to vent.
[6] Monitor the ripening of the fruit, comparing color changes in the bananas.
[7] Result: The banana in the container with the apples ripen faster.

(b) Explain this "experiment". What is happening? What difference do the apples make? (4 points)

(c) What is the purpose of step [5]? What would happen if this step would be skipped? (4 points).

(**d**) The formation of ethylene from ethanol is endothermic. Why does the reaction happen in the catalytic converters used in fruit ripening? (4 points)

(**e**) What is the function of the catalyst? You do not need to research which specific catalyst is used in these generators. Think about what function the catalyst needs to provide and then suggest a reasonable catalyst. (4 points)

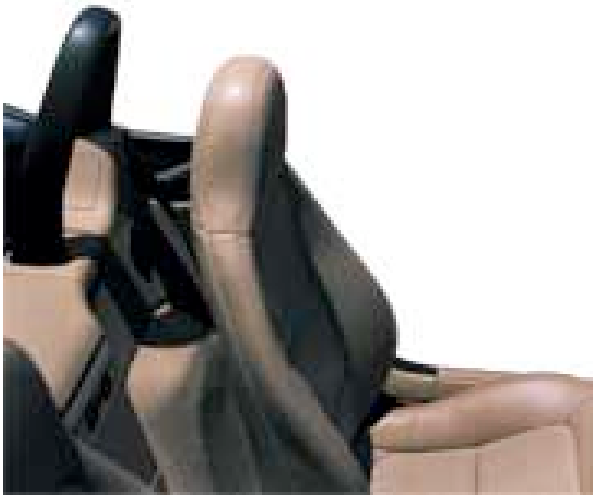
(**f**) Ethylene easily penetrates cardboard. Explain why ethylene has this welcome property. [Cardboard is made of polysugars; polar compounds with lots of alcohol groups.] (4 points)

Question 2. Polyethylene and PETROLITE® Copolymers (30 points)

(a) Consider the mechanism of acid-catalyzed addition of water to ethylene. Write down the complete reaction mechanism. Use sulfuric acid. Show every reaction intermediate. Show complete structural formulas; all atoms, all bonds, all valence electron pairs, formal charges, overall charges). Use the correct reaction arrows. Use curved arrows to indicate electron flow. Pay attention to detail. (10 pts)

(b) Consider the acid-catalyzed reaction of water with lots of ethylene. In this situation, the initially formed cation (protonated ethylene) will be more likely to add ethylene (rather than a water molecule) and a new cation is formed. This cation again has a choice between reacting with ethylene or water... Eventually, the long chain cation will add water and lose a proton. Let's consider the entire process that leads to the ethylene "tetramer". (Note: It's not really a tetramer; it's the tetramer plus water.) Draw complete structures; in this part (b) you may use condensed structures in the less interesting parts of the molecules. (10 points)

Structure of protonated ethylene:
Structure of the cation formed by addition of protonated ethylene to ethylene:
Structure of $C_6H_{13}^+$:
Structure of $C_8H_{17}^+$:
Structure of Structure of $C_8H_{17}OH$:



(c) Polyethylene (PE) is used for pipes and cutting boards; **PE is hard**. What a sharp contrast to the softness of PETROLITE® Copolymers used to make car seat covers. And this remarkable difference is due to just a few methyl groups. The copolymer is made by the polymerization of ethylene with some propylene. Let's see what the consequence of this small change is. Let's consider the "tetramer" (e.g. the tetramer plus water) of part **(b)** and draw all possible constitution isomers of the tetramer formed by three ethylene molecules and one propylene. (6 points)

Use line drawings!

(**d)** Why is PE hard while the copolymer is soft? A qualitative answer is requested. Cartoon drawings might help. (4 points)

Question 3. Industrial Alkene Formation (16 points)

Consider the **dehydration of *cis*-2-methylcyclohexanol with phosphoric acid, H_3PO_4.** Draw the structure of the substrate stereoisomer that has the *R*-configuration at the methyl-substituted C-atom. Use models as you need!

(a) Draw the substrate in the best possible fashion. Draw a chair form! Place methyl equatorial. (6 p.)

(b) Draw the structure of the protonated alcohol. (2 points)

(c) Draw the Zaitsev product. Indicate whether this alkene is *E* or *Z*. (4 points)

(d) Draw the Hoffman product. Indicate whether this alkene is *E* or *Z*. (4 points)

(a)	**(b)**
(c)	**(d)**

Question 4. Oxidations (18 points)

For each part, provide structures of the substrate, the specific reagents, and the products.
If there are several products, draw them all and indicate the major product.
Provide correct regiochemistry and stereochemistry if needed.

(**a**) Ozonolysis of *cis*-2-butene. (6 points)

(**b**) Epoxidation of *cis*-2-butene and subsequent acid-catalyzed hydrolysis. (6 points)

(**c**) Hydroboration-Oxidation of *cis*-2-butene. (6 points)

Question 5. Reductions (12 points)

For each part, provide structures of the substrate, the specific reagents, and the products.
If there are several products, draw them all and indicate the major product.
Provide correct regiochemistry and stereochemistry if needed.

(**a**) Reduction of 2-butyne to butane. (4 points)

(**b**) Reduction of 2-butyne to *cis*-2-butene. (4 points)

(**c**) Reduction of 2-butyne to *trans*-2-butene. (4 points)