Chemistry 2050 *Introduction to Organic Chemistry*
Fall Semester 2004, Dr. Rainer Glaser

Examination #3

"Radicals and Radical Chain Reactions. Alcohols, Ethers, Epoxides, and Aldehyde & Ketones."

Questions 1-3: Wednesday, 12/01/04, 11–11:50am.

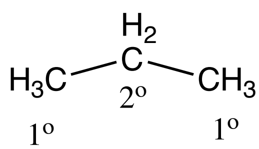
Questions 4 & 5: Submit Monday, 12/06/04, 11am.

Name: Answer Key

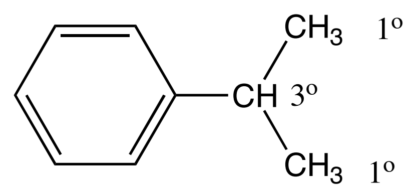
Question 1. Radical Chain Halogenation.	20	
Question 2. Hydroperoxides & Peracids.	20	
Question 3. Alcohols, Aldehydes, & Ketones.	20	
Question 4. Vitamin E.	20	
Question 5. Herman Mark, Polymer Chemist.	20	
Total	100	

Question 1. Radical Chain Halogenation. (20 points)

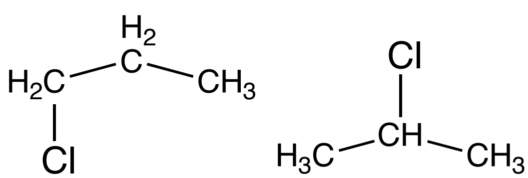
Draw the structure of **propane** and identify each carbon atom as primary (1°), secondary (2°) or tertiary (3°):



Draw the structure of ***iso*-propyl-benzene** and identify each carbon atom in the alkyl chain as primary (1°), secondary (2°) or tertiary (3°):



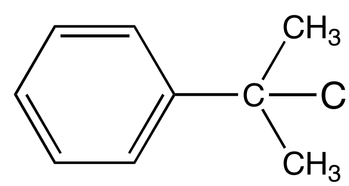
Major product of the photochemical monochlorination of **propane:**



Full credit for 1-chloropropane. Or Both.

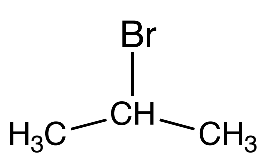
About equal amounts! Small selectivity.

Major product of the photochemical monochlorination of ***iso*-propyl-benzene**:



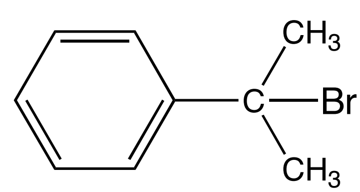
benzyl radical!

Major product of the photochemical monobromination of **propane**:



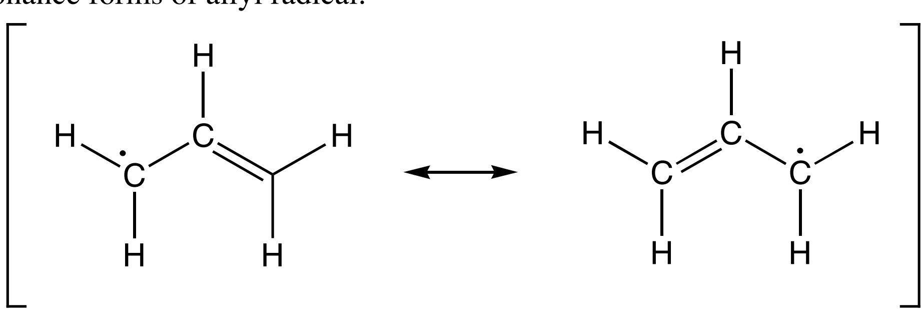
Br is very selective!

Major product of the photochemical monobromination of ***iso*-propyl-benzene**:



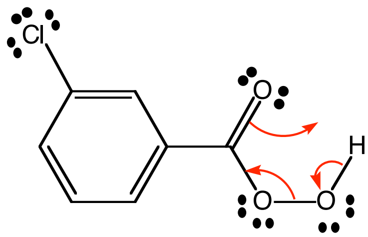
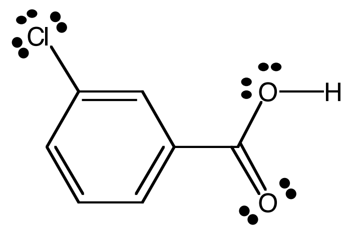
benzyl radical!

Draw both resonance forms of allyl radical:



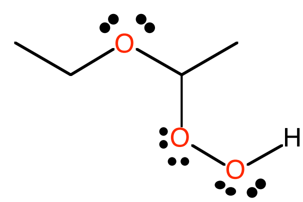
Question 2. Hydroperoxides & Peracids. (20 points)

(**a**) MCPBA is a standard reagent used for the delivery of "atomic oxygen" in epoxidations. Draw the complete Lewis structures (all bonds and lone pairs) of MCPBA and provide its full name. Draw the acid formed by release of oxygen and provide its full name as well. (6 points)

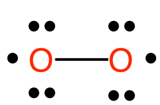
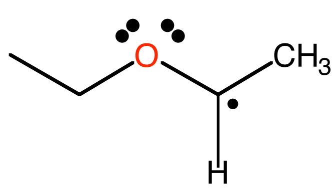
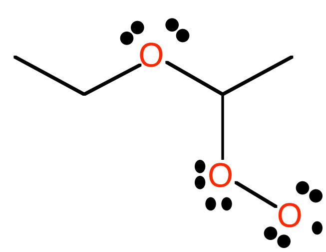
MCPBA: ***meta*-chloroperbenzoic acid**	Full name of product: ***meta*-chlorobenzoic acid**
	

(b) In your drawing of the structure of MCPBA in (a), draw curved arrows to indicate the electron shifts that cause the release of "atomic oxygen" and the formation of *meta*-chlorobenzoic acid. (4 points)

(c) On standing in air, ethers form explosive ether hydroperoxides. Draw the hydroperoxide formed by the **air oxidation of diethylether**. The overall oxidation reaction is a ________________ (**addition**, elimination, substitution). (3 points)

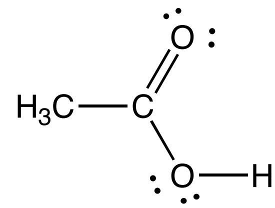


(d) The oxidation of diethylether is a **radical chain reaction** and molecular oxygen functions as the initiator and also as a reagent in one of the chain propagation steps. Draw the Lewis structure that reflects that molecular oxygen is a diradical. Draw the radicals formed by the reaction of O_2 with diethylether and in the O_2 addition step in the chain propagation. (1+3+3 points)

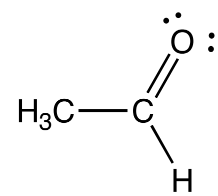
Molecular Oxygen	Radical formed by reaction of O_2 with diethylether	Radical formed in the O_2 addition step of the chain propagation
		

Question 3. Alcohols, Aldehydes & Ketones. (20 points)

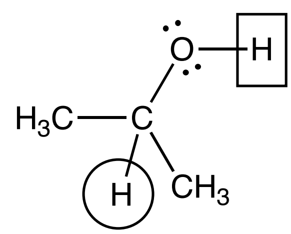
(a) The **oxidation of ethanol** with CrO_3 in sulfuric acid yields _____**(acetic) acid**___ as the final product. Draw the structure of the final product. (3 points)



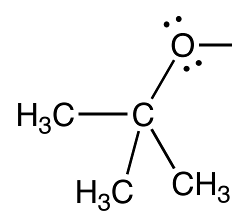
(b) The **oxidation of ethanol** with PCC (and in the absence of water!) yields ___**(acet)aldehyde**____ as the final product. Draw the structure of the final product. Provide the full name of PCC: __**pyridinium**_ _**chlorochromate**. (5 points)



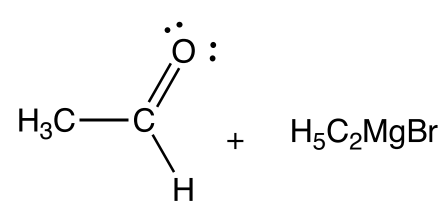
(c) Draw the structure of the product formed by **$LiAlH_4$ reduction of acetone**. Draw the final product, that is, the product obtained after quenching with water. Circle the "H" that comes from the hydride and draw a square around the "H" that comes from water. (4 points)



(d) Draw the structure of the alcohol formed in the **Grignard reaction** between **acetone** and **methyl magnesium bromide** in ___**ether**___ (suggest a solvent). The absence of water is very important because otherwise the carbanion is lost as the gas ____**methane**___. (5 points)



(e) Provide substrate and reagent for the synthesis of **2-butanol by way of a Grignard reaction**. If there are several options, it suffices to provide one of them. (3 points)



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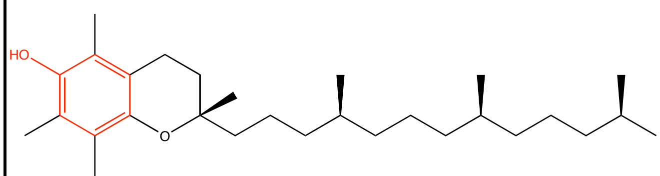
Question 4. Vitamin E. (20 points)

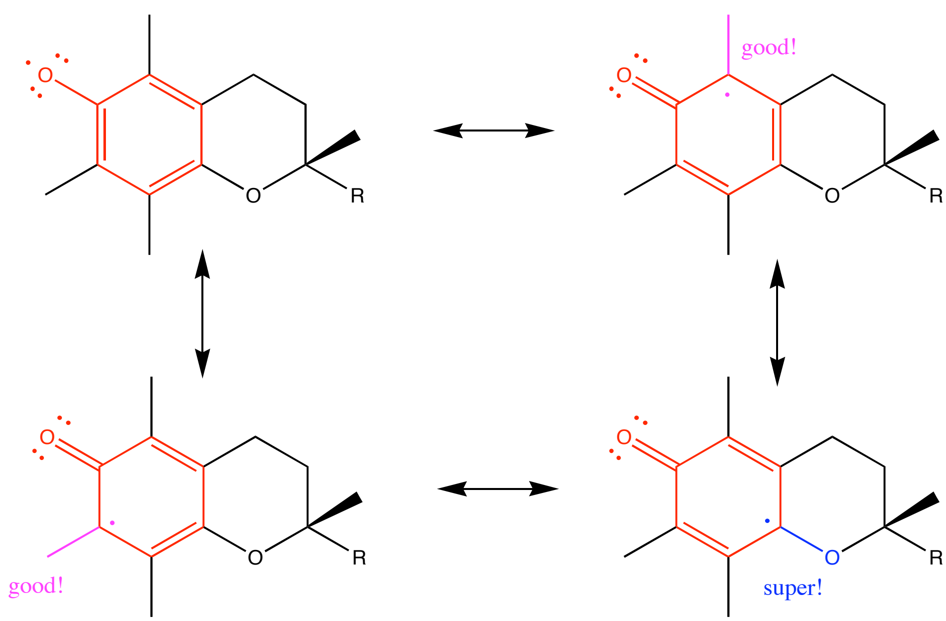
The following text appears on a web site by Michael W. Davidson, Florida State University: **"**Vitamin E was the fifth vitamin discovered when researchers found that a dietary deficiency in laboratory rats produced fetal death in pregnant females. The name "tocopherol" was derived from the Greek words for childbirth (***tos***), to bring forth (***phero***), and the chemical designation for an alcohol (***ol***). Vitamin E acts as a co-enzyme in cellular membranes and serves as a scavenger for free radicals that are destructive to the membrane and internal cellular components. Natural sources of vitamin E are vegetable oils, sunflower seeds, almonds, and peanuts."

Find the structure of Vitamin E in your textbook or elsewhere and draw its complete structural formula. Indicate which H atom is abstracted by a reactive radical. Draw the structure of the radical formed by H abstraction, draw as many resonance forms of the radical as needed, and explain why this new radical is less reactive (a "coach potato radical").

(a) Vitamin E Structure (4 points)



(b) Radical of Vitamin E (6 points)



Editorial: The Hazards of Vitamin E

The New York Times, November 14, 2004

Millions of Americans take big doses of vitamin E with the unproved assumption that the dietary supplement will improve their health. Now it turns out that large doses may actually be harmful.

That perplexing news was delivered by researchers from Johns Hopkins medical institutions last week, in a scientific talk and medical journal article that combined and reanalyzed the results of 19 studies involving some 136,000 people in North America, Europe and China. The researchers concluded that daily doses of 400 international units and above, the amount typically contained in vitamin E capsules, slightly increased the risk of dying from all causes. Those who took the high doses experienced 39 additional deaths per 10,000 people compared with those who took no supplements.

There are reasons to be cautious in generalizing these findings. Some statisticians find the pooling of results from disparate studies unpersuasive. Most of the patients were elderly people suffering from chronic illnesses, so the relevance to younger and healthier people is uncertain. The dose of vitamin E in a typical multivitamin pill, about 30 units, is far below the apparent danger zone.

Yet the findings should sound a cautionary note for millions of people who swallow big-dose vitamin E capsules as an antidote to ward off heart disease, cancer, Alzheimer's and even the common cold. There is scant evidence to support the presumed benefits, and now there is a signal of potential harm.

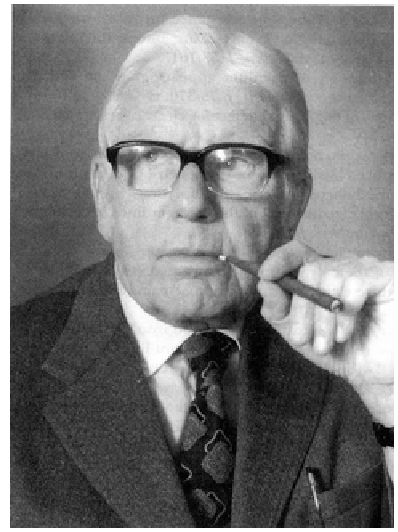
(c) How much is one international unit of vitamin E in grams? Provide the answer and the source for your answer in proper format please. [Zero points for the wrong answer even if you have a "source" for the wrong answer.] (4 points)

Answer suggested by Ann Notwehr: ATE = alpha tocopherol equivalents. IU = International unit. 1 mg ATE vitamin E = 1.5 IU. Or 1 IU vitamin E = 0.67 mg Source: http://ods.od.nih.gov/factsheets/vitamine.asp [accessed 12/4/2004]

(d) List **two** food items you eat daily to support your vitamin E needs. Provide estimates of how much you eat of each food item and how much vitamin E (in International Units) you ingest from each source. (6 points)

Item 1: Almonds	Amount consumed: 1 ounce	Vitamin E content: 7.4 mg or ca. 12 IU
Item 2: Broccoli	Amount consumed: 1 cup per week	Vitamin E content: 1.2/7 = 0.2 mg or 0.3 IU

Question 5. Herman Mark, Polymer Chemist. (20 points)



The New York Times, April 10, 1992, Friday, Late Edition - Final
NAME: Herman F. Mark
SECTION: Section B; Page 9; Column 1; National Desk
LENGTH: 784 words

HEADLINE: Dr. Herman F. Mark Dies at 96; A Pioneer in Polymer Chemistry

BYLINE: By WOLFGANG SAXON

BODY:

Dr. Herman F. Mark, a chemist who was a leader in research on polymers, giant long-chain molecules used in plastics and other materials affecting nearly all facets of life, died Monday in Austin, Tex. He was 96 years old and moved to Texas two years ago from Brooklyn, where he was dean emeritus of Polytechnic University.

Dr. Mark died after a brief illness at the home of his son, Dr. Hans M. Mark, chancellor of the University of Texas system, a statement from the university in Austin said.

For more than 75 years, Herman Mark was in the forefront of polymer chemistry. Polymers, which can be both natural and man-made, are used in materials like plastics, fibers and films, as well as biological chemicals and materials.

Papers, Books and Medals

Professor Mark wrote more than 600 research papers and some 40 books on polymer chemistry. He was the recipient of scores of medals and honorary degrees. His many awards included the National Medal of Science of the United States, the Humboldt Medal of Germany, the Wolf Prize of Israel, the Legion of Honor of France and the Honor Cross for Arts and Sciences of his native Austria.

Herman Francis Mark was born May 3, 1895, in Vienna, the son of a prominent physician. He served as a decorated combat infantry officer in the ski troops of the Austrian Army for four years in World War I.

His career began in 1921 when he received a Ph.D. in organic chemistry at the University of Vienna. That year, he also married Maria Schramek and moved to Berlin to take a post at the Kaiser Wilhelm Institute for Physical Chemistry. Albert Einstein was only one of the prominent scientists at the institute then.

In Berlin, Professor Mark developed the basic research processes from which his reputation subsequently grew. He did so by applying the techniques of modern physics to the study of large molecules.

In 1928, he became director of the research laboratory of I.G. Farbenindustrie, the chemical conglomerate, in Friedrichshafen. There, he and his associates worked out the structure of the natural polymer molecule, as in cellulose, silk, cotton, wool and protein. It was the first time that the structure of an organic polymer in living things had been accurately defined.

While involved in this research he was also teaching at the Technical University in Karlsruhe, where his students included Edward Teller, Leo Szilard and Eugene P. Wigner.

When the Nazis took over in Germany in 1933, Professor Mark accepted an offer to become professor of chemistry and director of the Chemical Institute of the University of Vienna. His major contribution there was to explain the behavior of a natural polymeric substance like rubber. He and his student Eugene Guth developed what today is known as the kinetic theory of rubber elasticity.

Under his leadership, polystyrene, a tough, clear, colorless plastic, and the first two synthetic rubbers were advanced toward commercial production.

Another accomplishment was the Mark-Houwink equation, which became the basis for the measurement of molecular weights of polymers.

Move to Brooklyn

The annexation of Austria by Nazi Germany in 1938 prompted Professor Mark to start a journey that ended three years later in Brooklyn where he accepted a professorship at the Polytechnic Institute, now Polytechnic University.

During World War II, he helped government agencies with projects involving synthetic rubbers, fibers and films.

In 1944, the Polymer Institute was established at Polytechnic with him as its first director. It became a center for polymer research in the United States and achieved a systematic understanding of the mechanical properties of polymers.

This enabled scientists to predict these properties and to tailor such substances to their intended use. That, in turn, made possible thousands of new plastics, fibers, paints and other materials produced by industry.

Professor Mark left the directorship in 1961 to become dean of the faculty of Polytechnic. He became emeritus dean, professor and trustee in 1964. Professor Mark remained active in research and scholarly endeavors. In the 1980's, for instance, he led a study of fire- and temperature-resistant polymers used in aircraft, hotels and other public facilities. A member of the National Academy of Sciences, he also headed an academy panel in 1984 that reviewed the space program's use of high-temperature-resistant materials in rocket nozzles.

Besides his son, Professor Mark is survived by a sister, Elizabeth Czitary of Vienna; three grandchildren and three great-grandchildren. His wife died in 1970.

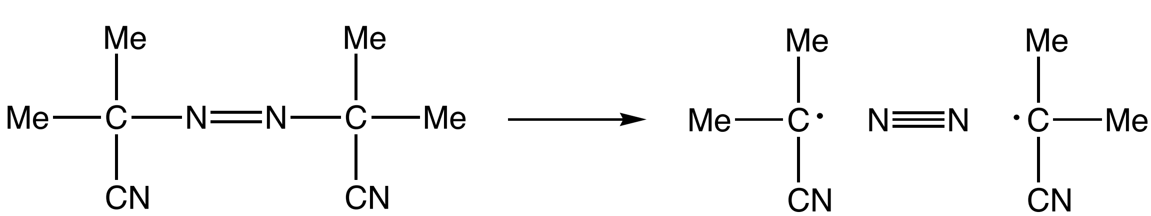
A memorial symposium will be held on the Brooklyn campus of Polytechnic in the fall.

GRAPHIC: Photo: Dr. Herman F. Mark. (The New York Times, 1975)

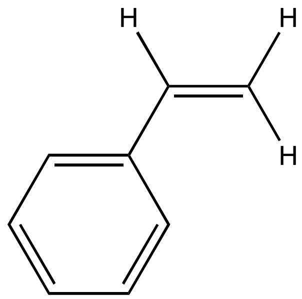
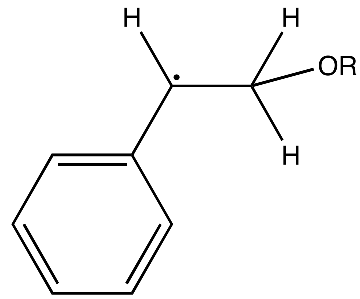
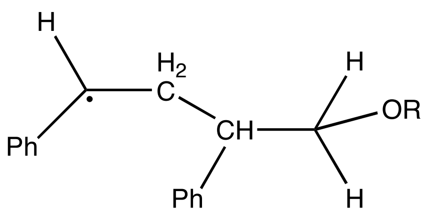
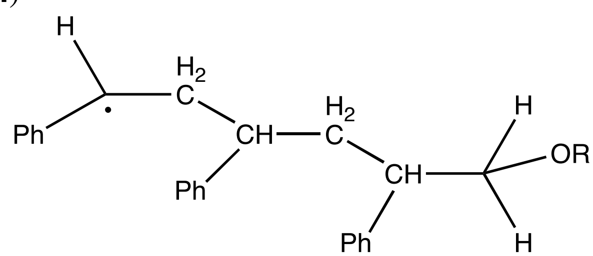
LOAD-DATE: April 10, 1992

Source of Art: http://www.nap.edu/readingroom/books/biomems/hmark.html

(a) Find the structure of the radical chain initiator 2,2-azo-bis-isobutyronitrile, draw the structure, and show the initiation reaction (e.g. how it forms radicals). (6 points)

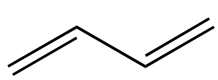


(b) Draw the structure of styrene **1**, of the product **2** formed by addition of RO-radical to styrene, of the product **3** formed by addition of styrene to **2**, and of the product **4** formed by addition of styrene to **3**. (8 points)

(**1**) 	(**2**) 
(**3**) 	(**4**) 

(c) What is "synthetic rubber"? Find out. Draw the monomer and give its name. Draw the rubber tetramer. When drawing the tetramer, use RO as the initiator and also as the piece added to terminate the tetramerisation. (6 points)

Monomer:



butadiene and derivatives

Tetramer: