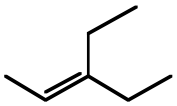
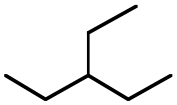
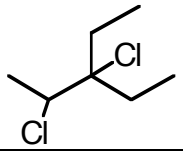
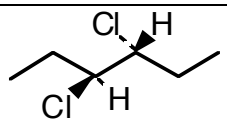
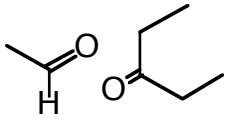
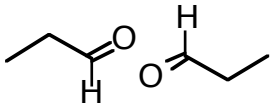
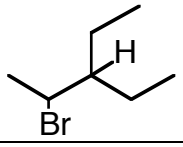
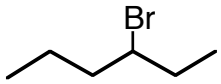
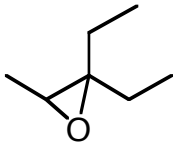
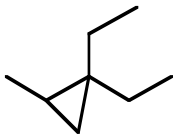
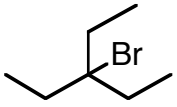
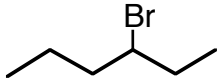
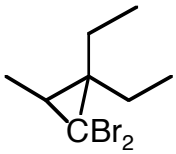
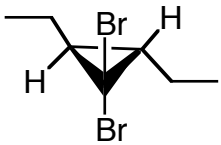
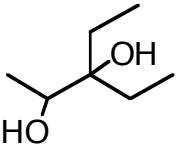
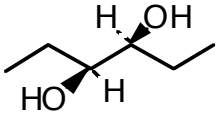
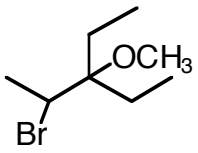
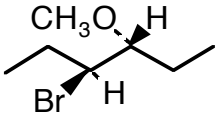
Chemistry 125 Sixth Examination Answers **March 3, 2004**

1. (12 min) Complete the following table by drawing under each alkene the structure of the product(s) expected from treating it with the reagents shown in the left column. (The first row is worked as an example. **No mechanisms** are necessary, just product structure. Be sensitive to **stereochemistry**, when it is relevant.)

Note that this question repeats the homework (Chapter 11, questions 6 and 7)

Reagent		
H_2 / Pd-C		
Cl_2 in CCl_4 at 0°C		
(1) O_3 (2) Zn dust, aq. HOAc		
HBr / peroxides		
peroxybenzoic acid in chloroform	 (racemic)	 (trans,racemic)
CH_2I_2, Zn(Cu), ether	 (racemic)	 (trans,racemic)
HBr, free-radical inhibitor		
$CHBr_3$, *t*-BuOK, *t*-BuOH	 (racemic)	 (trans,racemic)
cold dilute $KMnO_4$	 (racemic)	 (racemic)

Br_2, dilute soln. in CH_3OH	 (racemic)	 (racemic)

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2. (6 min) **Explain one** of the following (Choose A or B).

A) How magnetic resonance can be used to image which section of the brain is active during a particular thought process.

or

B) Whether a top should precess faster or slower as its rate of spinning about its axis slows.

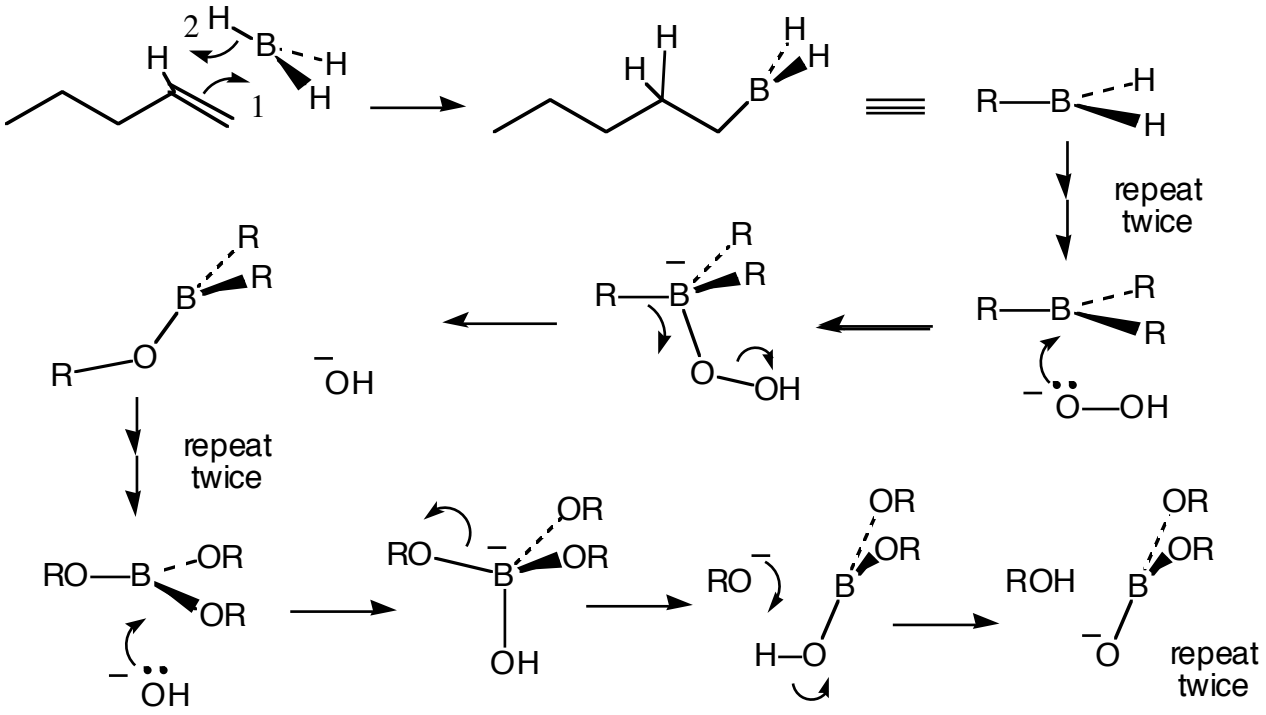
A) By placing the subject in various inhomogeneous magnetic fields, the source location of proton NMR signals can be determined by the precession frequency (3 pts). Active regions of the brain have increased blood flow. Increased blood flow results in higher oxygen levels (4 pts). Since molecular oxygen is magnetic, it interacts with magnetic H nuclei of water and causes them to relax more easily, increasing the local nmr signal strength (3 pts). Comparing MRI images before and after the mental activity shows where the activity occurs (2 pts). [This is called BOLD imaging]

See http://classes.yale.edu/chem125a/125/spectroscopy/nmr/Relaxation/Relaxation.htm

B) When gravity attemps to twist a spinning top, the response of a point on the surface of the top lags the force from the twist by 90° rotation, maximum response comes 1/4 turn after maximum force, resulting in precession rather than twist toward the ground (6 pts). Slower spining of the top gives a longer time to integrate, or “sum up”, the force that reslts in precession, therefore resulting in faster precession (6 pts). [A top precesses faster and faster as its spinning slows.

See http://classes.yale.edu/chem125a/125/spectroscopy/nmr/Precession/precession.htm

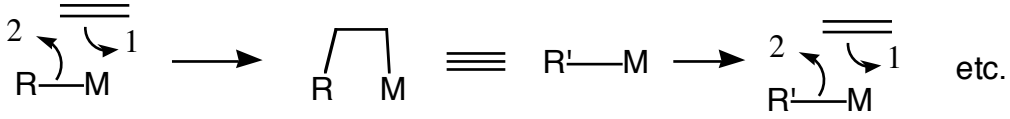
3. (6 min) Used curved arrows to draw the mechanistic steps involved in achieving "anti-Markovnikov" addition of the elements of water (H and OH) to 1-pentene.



When drawing curved arrows, be careful that they begin at the location of the electron pair (HOMO) in the starting material and are directed to generate overlap with the LUMO so as to terminate where the electron pair is located in the product (bond or unshared pair). Don't make too many things happen at once, unless they truly do happen at exactly the same time. Here we have shown every intermediate in the reaction scheme (and have used 1 and 2 in the first reaction to indicate that one bond is probably forms more quickly than the other (to explain "anti" Markovnikov) but that there is not a delay before the second bond begins to form (to explain "syn" addition). Keep track of charges.

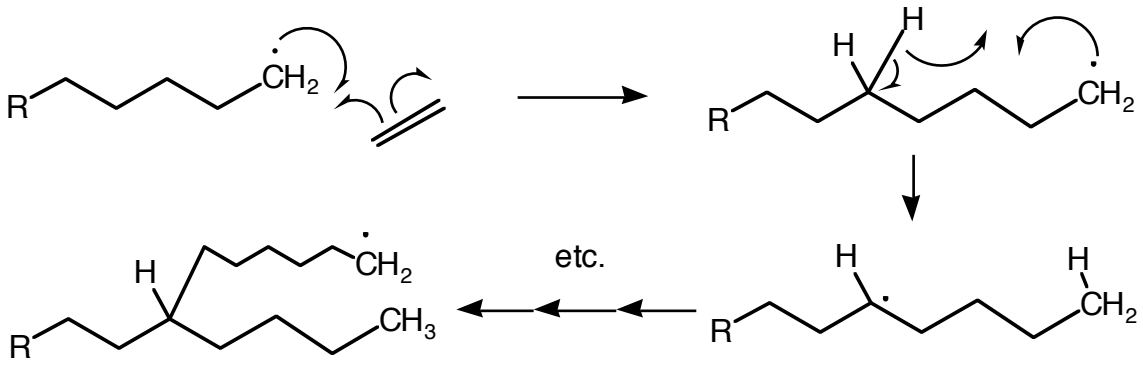
4. (8 min) When I added oil to my car engine yesterday, I noticed that there was a recycling symbol stamped on the plastic oil container. It said "HDPE", meaning high density polyethylene. Briefly describe the chemical process used to make HDPE **and** the process used to make LDPE **and** explain why the densities of the materials differ.

HDPE is made by "anionic" (more properly organometallic, or Ziegler-Natta) polymerization of ethylene, which gives a strictly linear molecular chain of (CH_2) groups. (6pts)



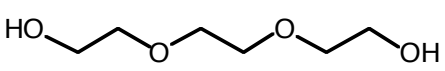
[Note that it is not possible to use cationic polymerization with ethylene, because it would be too slow to form the necessary primary cations (substituted alkenes – styrene, etc. – would not yield poly(ethylene) but rather poly(styrene), etc.]

LDPE is made by free-radical polymerization, during which it occasionally happens that the primary radical reaches back and abstracts an H-atom from the growing chain to form a secondary radical, which ultimately adds another ethylene and create random branches in the molecular chain. (6pts)

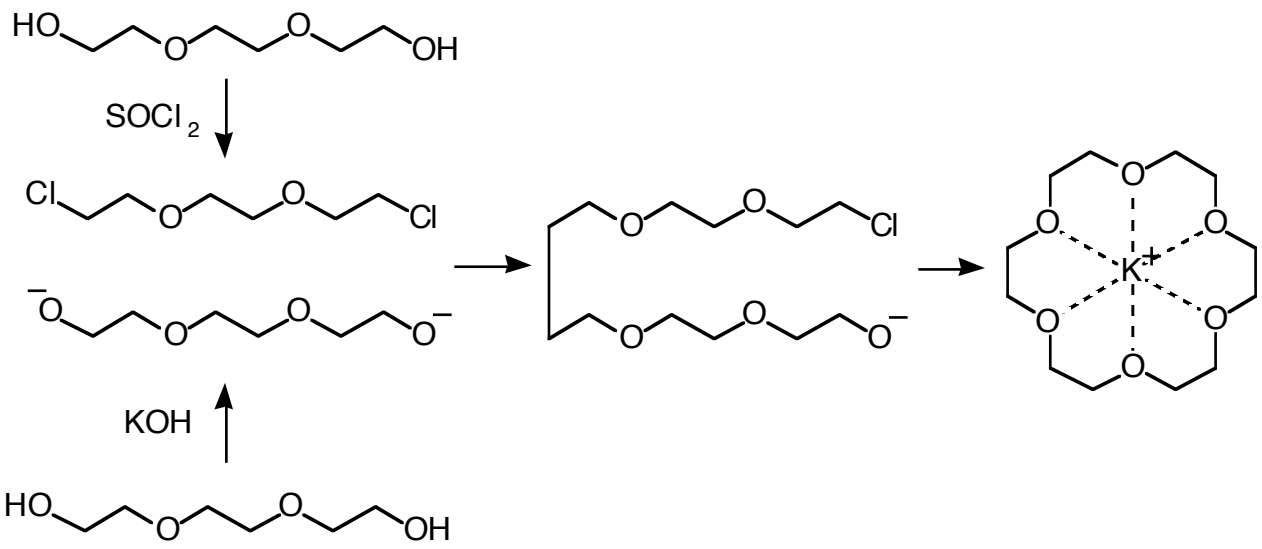


The strictly linear HDPE chains pack together more efficiently to give a denser, and more crystalline PE than is available with the randomly branched chains of LDPE. (4 pts)

5. (5 min) A sample of triethylene glycol (right) can be dimerized by treating half of it with excess $SOCl_2$ and reacting the remainder with the product of the $SOCl_2$ reaction in the presence of aqueous KOH. The dimer product of this process can be used to dissolve $KMnO_4$ in a hydrocarbon solvent.



Explain two ways in which KOH facilitates this dimerization, and why it is better than NaOH for this purpose.



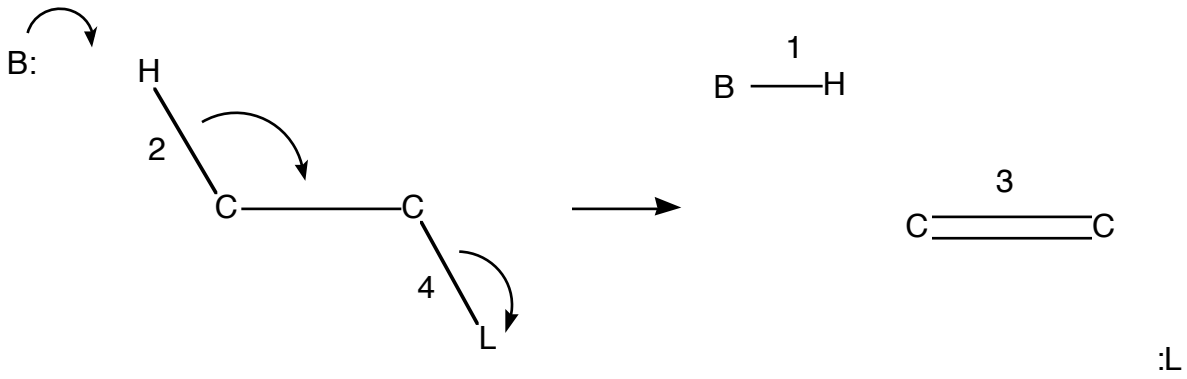
KOH helps this reaction both by abstracting protons from the OH groups to create the alkoxide nucleophiles for the two S_N2 reactions, and by serving as a template to bring the ends of the long intermediate chain together for the second S_N2 reaction. Like Goldilocks,

potassium fits just right inside the 18-Crown-6 ether. Sodium is too small to fit properly and position the ends to react.

6. (1 min) Give approximate pKa values for CH_4 **(~50)** C_2H_4 **(~44)** C_2H_2 **(~25)** and NH_3 **(~34)**

7. (12 minutes) Provide experimental evidence to support the suggestion that in the transition state for E2 elimination two bonds are being broken and two bonds are being formed simultaneously. This will probably require four different kinds of evidence.

A perfect answer would supply specific experimental results.



Bond 1 is forming : Rate depends on concentration of Base (E2)

Bond 2 is breaking : Kinetic deuterium isotope effect on reaction rate (H faster than D)

Bond 3 is forming : Stereochemistry is “anti”

Bond 4 is breaking : Rate depends on nature of leaving group L (I > Br > Cl)