Name: _____

Chem 12A
September 26, 2011

Exam 1
show all work!!

Exam 1 is worth 10% of your grade (50 points). You are allowed to use **one** 3"x5" index card for notes. Show all work for full credit. Write your answers legibly. You may ask me for a hint; however, each hint will cost you 1 point.

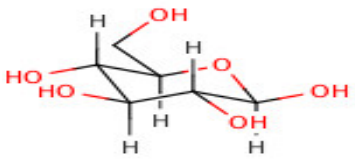
Acidity Constants (pK_a) of Acids.

Acid	HBr	HCl	$CH_3CH_2OH_2^+$	H_3O^+	H_2O	CH_3CH_2OH	CH_3CH_3
pK_a	-5.8	-3.9	-2.4	-1.7	15.7	16	62

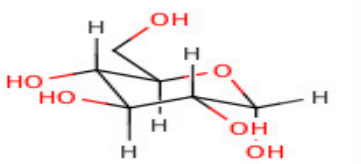
1. (4 points) Give a short answer to each question.
a. What is the difference between a σ bond and π bond?
b. What is the difference between a Lewis structure and resonance structure?
c. In terms of bond breaking/forming, what is the difference between a polar reaction and radical reaction?
d. In terms of stability, is it better for a (+) or (-) charge to be concentrated or spread out?

2. (4 points) Cyclohexane exists in the chair and boat conformation.
a. Draw the chair and boat conformers of cyclohexane. Circle the atoms that causes strain in each conformer.
b. Based on your answer to part (a), explain why the chair conformer is more stable than the boat conformer.

3. (4 points) Six sided rings are found in biomolecules. Two conformers of glucopyranose are shown below. Which conformer is more stable? Give reasons.

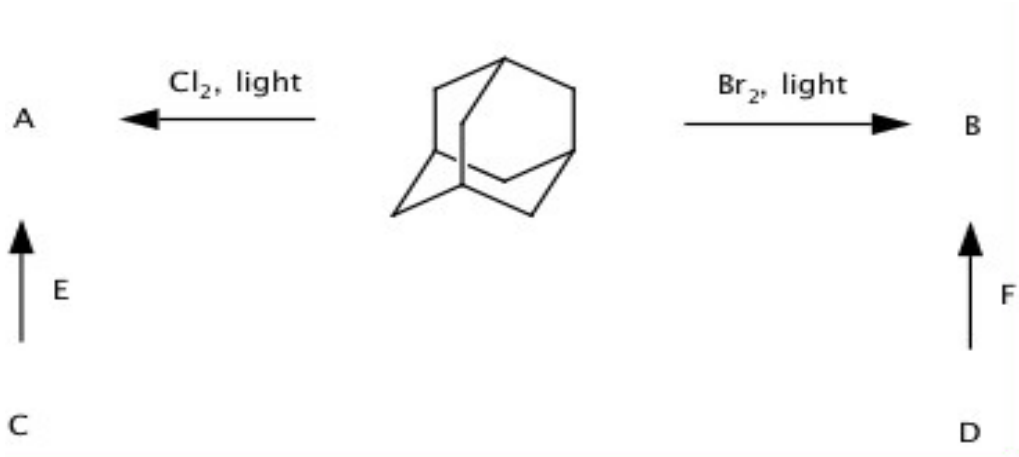


B-D-Glucopyranose

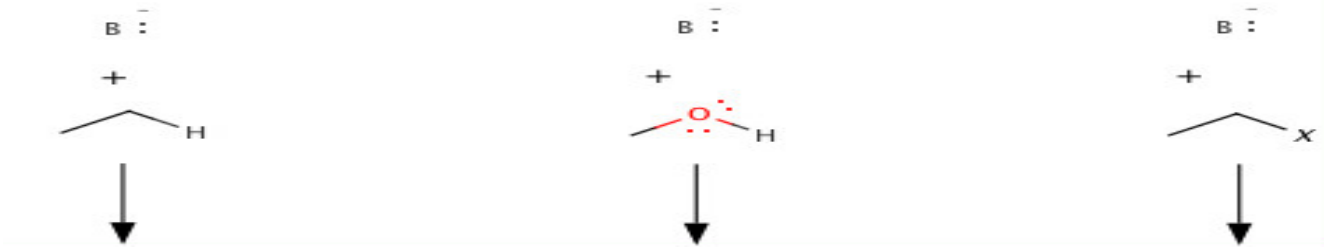


a-D-Glucopyranose

4. (16 points) 0.001 to 0.03% of petroleum contains adamantane (shown below in part (c)). The chemical formula of this colorless, crystalline cycloalkane is $C_{10}H_{16}$.
a. $C_{10}H_{16}$ has many isomers. What is the degree of unsaturation of $C_{10}H_{16}$? In other words, how many π bonds or rings or both are possible in $C_{10}H_{16}$? Draw one constitutional (structural) isomer of adamantane.
b. Carbons are classified as 1°, 2°, and 3°. Which carbon type is found in the highest amount in adamantane? Circle each of these carbon types in the structure below in part (c).
c. Predict the most likely product of each reaction with adamantane. Draw the structures of A and B.
Then, determine a second way to synthesize A and B by drawing the structures of C and D. State the reagents E and F for each reaction..

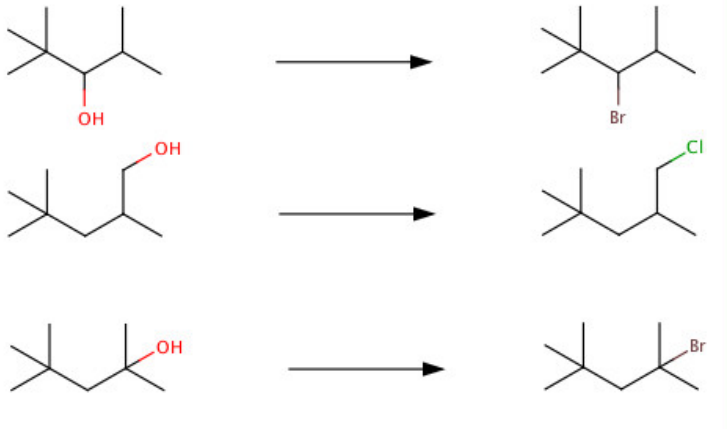


5. (10 points) So far in Chem 12A, we have looked at alkanes, alcohols, and alkyl halides.
a. These three functional groups can react with a base (nucleophile). Using curved arrows, show how a base ($B:^-$) reacts with each functional group. Draw the structure of the product of each reaction.



b. Other than B-H, which product from part (a) is the best leaving group? Give reasons.
c. Of the three functional groups in part a, which group(s) react(s) with an acid? Using curved arrows, show how the functional group reacts with an acid (H^+). Draw the structure of the product of your reaction(s).

6. (12 points) Alcohols undergo substitution reactions to form alkyl halides. HBr, $SOCl_2$, and PBr_3 are reagents used in these reactions.
a. Which reagent would you use in each reaction? Give reasons.



b. For the reaction that produces a 2^o alkyl halide, draw the Newman projection of the most stable conformer. Sight down the C2 – C3 bond. Is this conformer staggered, eclipsed, chair, boat, anti, syn, gauche, axial, or equatorial?

c. For the reaction in part (a) that proceeds by a S_N1 mechanism, describe the mechanism. For each step:
(i) determine the shape and valence bond hybridization at the C at which the substitution reaction occurs,
(ii) identify the nucleophile and electrophile,
(iii) use curved arrows to show bonds breaking and forming.

Name: _____

Chem 12A
November 9, 2011

Exam 2
Show all work!!

Exam 2 is worth 10% of your grade (50 points). You are allowed to use one 3"x5" index card for notes. Show all work for full credit. Write your answers legibly. You may ask me for a hint; however, each hint will cost you 1 point.

1. (14 points) So far in Chem 12A, we have looked at four functional groups (alkanes, alcohols, alkyl halides, alkenes) and at three reaction types (substitution reactions, elimination reactions, and addition).

a. Of the four functional groups, which group(s) undergo(es) elimination reactions?

b. Of the four functional groups, which group(s) undergo(es) addition reactions? What makes this functional group(s) want to undergo addition reactions?

c. Of the four functional groups, which group(s) contain(s) a leaving group?

d. Of these three reaction types, which reaction type(s) require(s) a leaving group in a reactant?

e. If you found more than one functional group that contains a leaving group, which functional group contains the better leaving group? Give reasons.

f. Consider the structure below. LG = leaving group. On this structure,

(i) circle the atom(s) at which an addition reaction occurs. Draw in H's as needed.

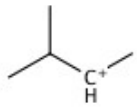
(ii) Draw a box around the atom(s) at which a substitution reaction occurs. Draw in H's as needed.

(iii) Draw a triangle around the atom(s) at which an elimination reaction occurs. Draw in H's as needed.

2. (10 points) Carbocations are intermediates in reactions that we have looked at in Chem 12A. Carbocations can do three things.

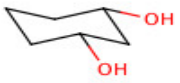
a. Show <u>two</u> different reactants and reaction conditions from which the carbocation shown below is made. (Note: changing from one halide to another is considered the same reaction.)

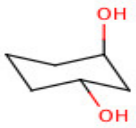
b. Show the <u>three</u> things that can happen to this carbocation. Use $Nu:^-$ if you want to show a nucleophile and E^+ if you want to show an electrophile. Draw the structure of each product formed. Use curved arrows to show bonds breaking and forming.



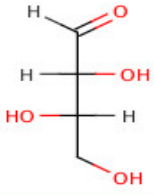
3. (6 points) Identify the following pairs as constitutional isomers, stereoisomers, or the same compound If they are stereoisomers, are they enantiomers or diastereomers?

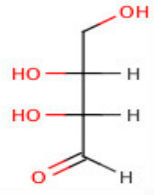
a.





b.

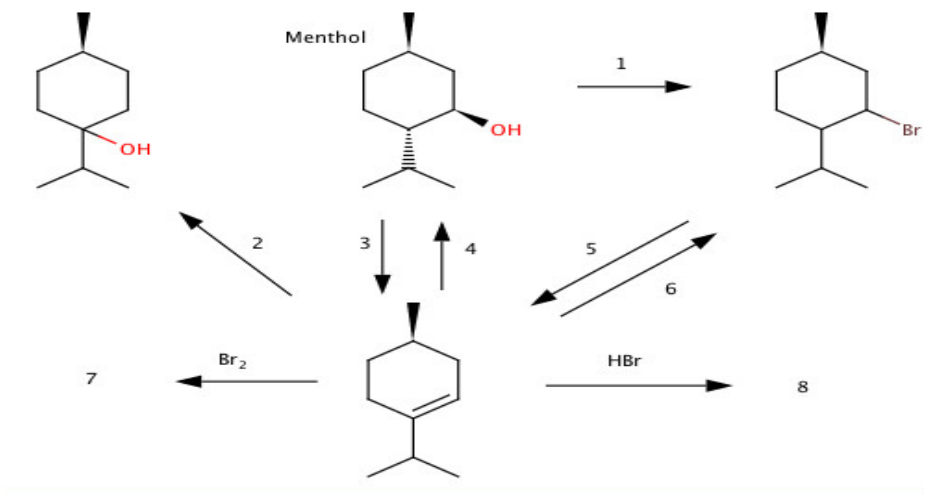




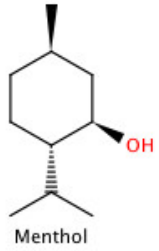
c. For one of the structures in part b, changing one group turns that compound into a meso compound. Change this group and draw the structure of the meso compound.

4. (20 points) Menthol is found in peppermint, is an anesthetic and counterirritant, and is used to soothe throat irritation.

a. Determine the reaction conditions for (1) through (6). Draw the structures of (7) and (8). You do not have to consider stereochemistry in your answers.



b. Is menthol optically active? If so, circle the chirality center(s) in the structure below. Determine the configuration (R or S) at each chirality center. How many stereoisomers does menthol have?



c. See Reaction (1) from part (a): menthol → menthyl bromide. Is menthyl bromide optically active? Give reasons.

d. See the reaction that produces (7) from part (a): Br_2 addition to 3-menthene. Is (7) a racemic mixture that is optically inactive? Give reasons.

Chem 12A Fall 2011 Lab Notebook and Lab Safety Factor
Due Wednesday, December 7, 2011

Your Lab Notebook and Lab Safety Factor Grade is worth 5% of your overall course grade.
1. For your lab notebook, give yourself a grade (A – F) based on the following criteria. Be honest and be fair to yourself. Don't be too easy but don't be too harsh either. Then, give yourself an overall lab notebook grade.

Criteria	Grade
Labs 1 through 11 entered in sequential order	
Each lab shows a flow chart, relevant chemical equations, properties, and calculations, table of data and results, discussion, and conclusions	
Appropriate details so another organic chemistry student can follow what you did in each experiment	
Overall Lab Notebook Grade	

2. For your lab safety factor grade, give yourself a grade (A – F) based on the following criteria. Be honest and be fair to yourself. Don't be too easy but don't be too harsh either. Then, give yourself an overall lab safety factor grade.

Criteria	Grade
Attendance (including being on time)	
Your timely submission of lab assignments	
Your observation of lab safety rules and regulations	
Your lab technique	
Your initiative and cooperation	
Overall Lab Safety Factor Grade	

3. **Combined** Lab Notebook and Lab Safety Factor Grade: _____

4. a. Do you believe the lab portion of this course helped you learn organic chemical reaction principles?
b. Ignoring poor product yields and not having an IR, which lab do you think was the most helpful in learning organic chemistry? Give reasons.
c. Which lab do you think was least helpful in learning organic chemistry? Give reasons.

Did you have enough or adequate help in this course (lecture or lab or both)? What could have made it better?

Chem 12A, FINAL EXAM - TAKE-HOME PART
due Wednesday, December 14, 2011 at 3:00 pm

The Take Home Part of the Final Exam is worth 10% of your grade (50 points). For full credit, show all work in a logical and legible sequence. Clearly underline or circle your final answer. Include units where needed. You may work in groups on Questions 1 – 5 of the Final Exam. **You must do Question 6 on your own.** If you work in a group, make sure every member contributes to the solutions. Turn in one set of solutions with the names of each member of your group. If you discuss any question or part of a question with another student, you are working in a group.

1. (10 points) A chemical formula tells you the number of atoms of an element in a compound but may not tell you the connectivity (bonding), functional group(s), or number of pi bonds or rings. We discussed degree of unsaturation in class.

a. We looked at alkanes, alkenes, alkynes, dienes, RX, and ROH in CHM 12A. For a chemical formula that contains a halogen, how is X treated in determining the degree of unsaturation? For a chemical formula that contains oxygen, how is O treated in determining the degree of unsaturation?

b. Determine degree of unsaturation of each chemical formula and draw two structural isomers.

(i) C_6H_6

(ii) C_3H_6O

(iii) $C_{10}H_6Cl_8$

c. For each pair of isomers in part b, describe how IR spectroscopy could be used to distinguish between each isomer. Sketch an IR spectrum of each compound. Identify the peaks and bond types that distinguishes one isomer from the other.

2. (15 points) Cholesterol is a steroid fat that is produced in the liver. Look up and draw the structure of cholesterol.

a. Is cholesterol flat? In other words, are all of the carbons in the rings in the same plane?

b. Circle the chirality centers. Is the carbon bonded to the alcohol group a chirality center? If so, determine the configuration (R/S).

b. Determine the number of stereoisomers of cholesterol.

c. Box the atom(s) at which an addition reaction can occur.

d. Triangle the atom(s) at which substitution can occur (polar, not radical).

e. Draw a hexagon around the atom(s) at which elimination can occur.

f. You eat food that contains cholesterol (from an animal source), which comes in contact with HCl in your stomach. Assume cholesterol reacts with an equimolar amount of HCl. Draw the structure of the major product of this reaction.

g. For the reaction in part f, would you expect a racemic mixture of product(s) or an enantiomeric excess? Give reasons.

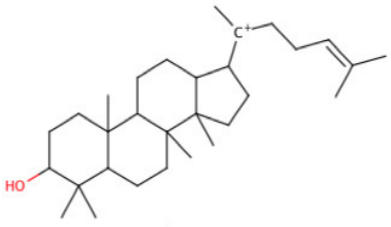
3. (7 points) Pesistant Organic Pollutants (POPs) are organic compounds that are resistant to environmental degradation through chemical, biological, and photolytic processes. POPs persist in the environment, are capable of long range transport, bioaccumulate in human/animal tissue, biomagnify in food chains and may have a significant impact on human health. Many POPs are halogenated, usually with chlorine.

a. Why are POPs persistent?

b. One POP is chlordane, which was used as an insecticide. Look up the structure of chlordane. Based on bonding and structure, what makes chlordane a POP?

c. Use a Chem 12A reaction that makes chlordane less of a POP. Describe the reaction conditions and product(s). Briefly explain why your product is less of a POP.

4. (5 points) In Lecture Slide 84, squalene undergoes a series of reactions to make lanosterol. Starting from the carbocation shown below, use curved arrows to show bonds breakng and forming in the two hydride shifts, two methyl shifts, and elimination reactions to produce lanosterol. Draw the structure of each intermediate.



5. (5 points) a. In Lecture Slide 123, methionine reacts with ATP to produce SAM in a substitution reaction. Elimination competes with substitution. Can an elimination reaction occur? If so, draw the structure of the product of the competing elimination reaction.

b. In Lecture Slide 124, SAM reacts with noradrenaline to produce adrenaline. what is the leaving group? Elimination competes with substitution. Can an elimination reaction occur? If so, draw the structure of the product of the competing elimination reaction.

6. (8 points) According to the Chem 12A Course Information Handout, your "grade will be based on your performance and mastery of the last Course Objective." Each course objective is shown below.
a. For each objective, give yourself a grade (A – F) that reflects your understanding of that objective. Be honest and be fair to yourself. Don't be too easy but don't be too harsh either
b. Identify the course objective that you understand the best. What did you do to help you understand this objective so well?
c. Identify the course objective that you understand the worst. What could you have done to understand this objective better?
d. The following terms were used in Chem 12A: inductive effect, steric effect, resonance stabilization, carbocation intermediate, regioselective, stereoselective, stereospecific, activating/deactivating group. Match the term to the appropriate course objective. Give one example of how this term is associated with this objective.
e. Give yourself an overall course grade based on your understanding of the course objectives. (The grade you give yourself may not be your official course grade. Your instructor will determine your overall course grade.)

Objective	Description	Grade
1	Draw Lewis and skeletal structures of organic compounds	
2	Name and classify organic compounds by functional group; identify their physical and chemical properties, especially reactivity trends	
3	Identify common nucleophiles and electrophiles and be able to rank by strength	
4	Determine and compare stability, e.g., resonance, of organic compounds and apply to reactions	
5	Relate structure and reactivity to stereochemistry. Draw Newman and Fischer projections	
6	Apply (2), (3), (4), and (5) to predict products of organic reactions given reactants and reaction conditions given products	
7	Design syntheses of organic compounds	
8	Describe organic reaction mechanisms by type, identify common organic mechanistic processes, and use curved arrows to show bonds breaking and forming	
9	Perform organic laboratory techniques to separate, isolate, and identify organic compounds	
10	Identify and distinguish between different characterization methods, e.g., IR, for organic compounds	
	Overall Chem 12A Grade	

c. Take the following survey: http://www.surveymonkey.com/s/HDNZ59G
(i) Briefly explain your answer to Question 1.

Name: _____

Chem 12A
December 14, 2011

FINAL EXAM
Show all work!!

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Acidity Constants (pK_a) of Acids.

Acid	HBr	HCl	$CH_3CH_2OH_2^+$	H_3O^+	H_2O	CH_3CH_2OH	CH_3CH_3
pK_a	-5.8	-3.9	-2.4	-1.7	15.7	16	62

1. (8 points) Draw the most stable structure of hexane, hexadiene (show the specific position of each pi bond), cyclohexane, and cyclohexene. Use a Lewis structure, Newman projection, sawhorse, or Fischer projection as needed. Identify each structure by name, e.g., staggered, as needed.

2. (12 points) We studied alkanes, alkenes, alkynes, dienes, allylic compounds, alcohols, and alkyl halides in Chem 12A this semester.

a. Rank a simple alkene, conjugated diene, and alcohol in order of nucleophilic strength. Give reasons for your ranking.

b. You want to make rubbing alcohol (2-propanol) from an appropriate alkyl halide. Briefly explain the reaction conditions (nucleophile, substrate, and solvent) you would use to maximize the yield of the alcohol and minimize the yield of the elimination product.

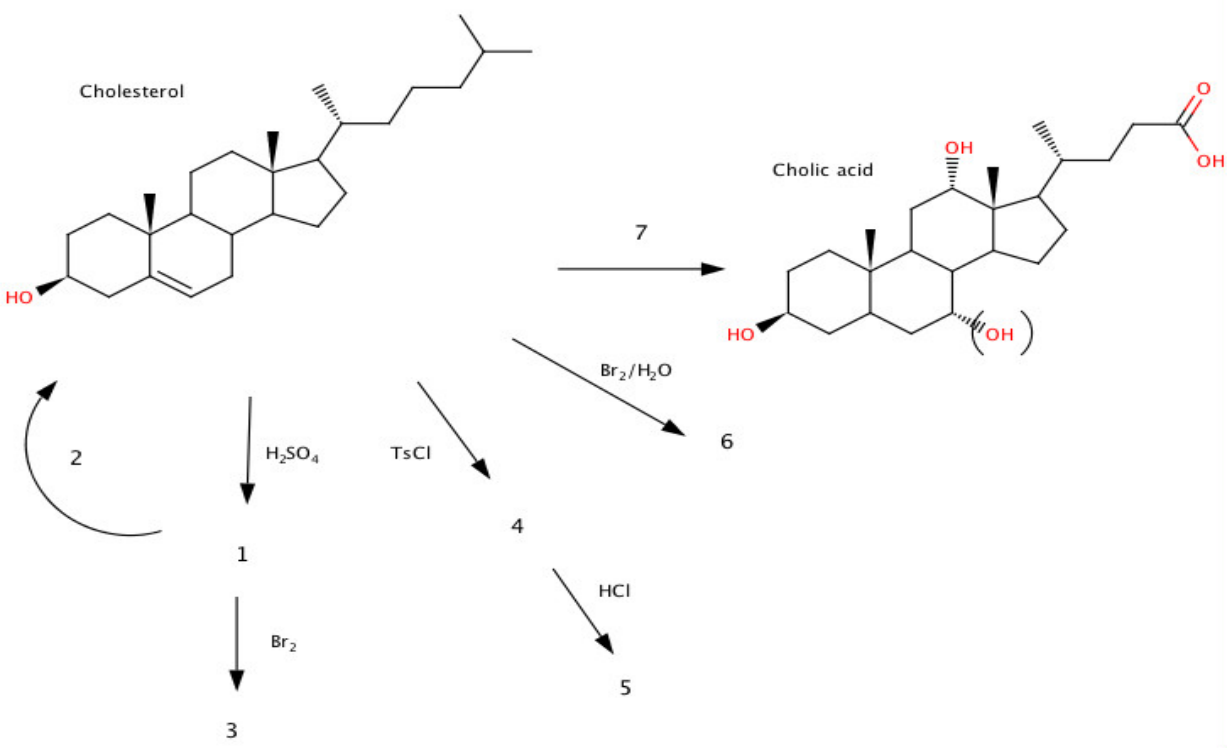
c. Is there another way to make rubbing alcohol which gives a better yield? If so, how would you do so?

3. (20 points) Cholesterol is a steroid fat that is needed to build and maintain cell membranes.
a. On the structure below, circle the α–carbon(s), box the β–carbon(s), triangle the vinyl carbon(s), and diamond the allyic carbon(s). Which atom is the best nucleophile in cholesterol?

b. Draw the structure or identify the reaction conditions for (1) through (7).
(i) To make compound (4), tosyl chloride (TsCl) reacts with –OH. The resulting product makes
- the –OH group into a better _____ group. Name another way to make –OH into a better _____ group.

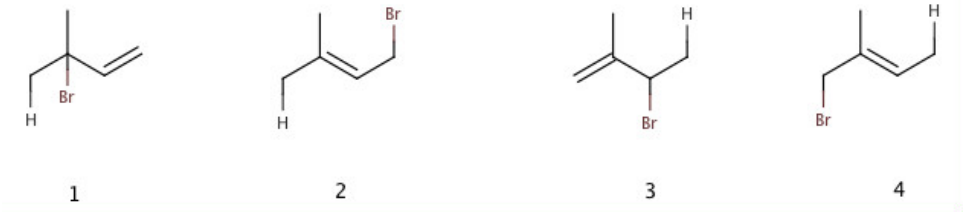
- In compound (4), the tosyl compound also serves as a *protecting* group. If a compound has an -OH group and another functional group and you don't want a reaction to occur at the –OH but want a reaction to occur at the other group, the –OH group is treated with TsCl. The resulting group is much less reactive than the –OH and allows the desired functional group to undergo the reaction you want.

(ii) For Reaction (7), cholesterol is converted into cholic acid, which is one of the two major bile acids produced in the liver. Focus on the –OH group in parenthesis. For this reaction, ignore the other -OH groups.



4. (10 points) Isoprene (2-methyl-1,3-butadiene) is an important starting material to make neoprene rubber.
a. Starting from ethylene, design a synthesis of isoprene. You can use any necessary inorganic and organic reagents.

b. When isoprene reacts with HBr, 1 and 2 are produced rather than 3 and 4. Explain this product distribution with a reaction mechanism. Use curved arrows to show bonds breaking and forming.



1 2 3 4