

Chemistry 210
Winter Semester 1997
Examination #3

Prof. Rainer Glaser , University of Missouri—Columbia
Wednesday, April 16, 1997, in Ellis Auditorium, 8:40 - 9:30

featuring
Nucleophilic Substitutions and Eliminations,
and the Chemistry of Alcohols

Your Name: <p style="text-align: center;">Answer Key</p>
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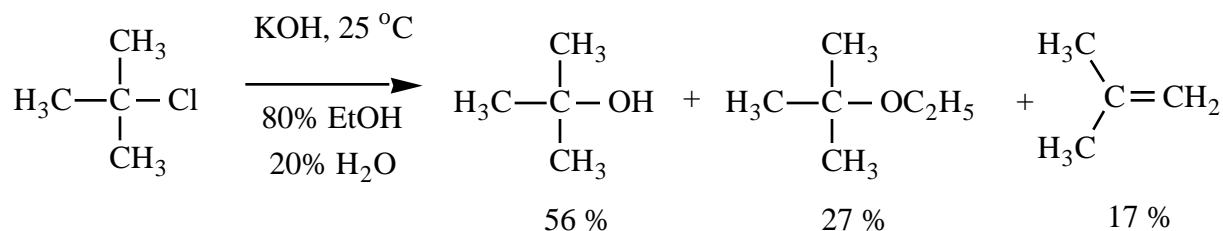
	Max.	Yours
Question 1 (S&E)	25	
Question 2 (more E)	26	
Question 3 (alcohols)	25	
Question 4 (ethers)	24	
Total	100	



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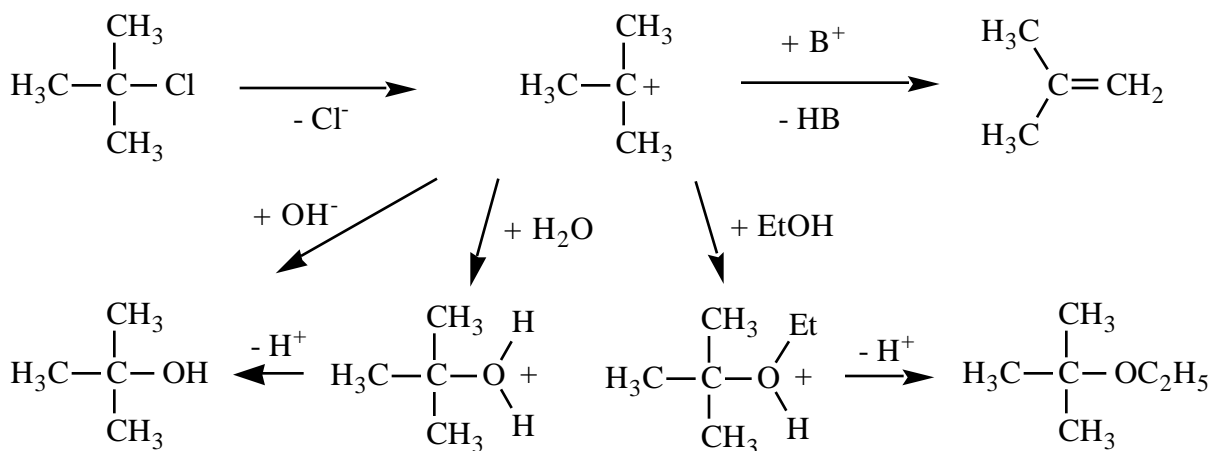
Question 1. Nucleophilic Substitutions and Eliminations. (25 points)



The reaction of *tert.*-butyl chloride with KOH in 80 % ethanol / 20% water at room temperature affords the three products shown. The kinetics of the reaction were measured and it was found that the reaction is first order in *tert.*-butyl chloride and that the reaction is independent of the KOH concentration.

(a) Based on the information, it is clear that the alcohol is formed in an $\text{S}_{\text{N}}1$ ($\text{S}_{\text{N}}1$, $\text{S}_{\text{N}}2$) reaction, that the ether is formed in an $\text{S}_{\text{N}}1$ ($\text{S}_{\text{N}}1$, $\text{S}_{\text{N}}2$) reaction, and that the alkene is formed in an $\text{E}1$ ($\text{E}1$, $\text{E}2$, $\text{E}1\text{cB}$) reaction. Provide a **complete reaction mechanism** that explains all three products.

(6 points for filling in the blanks, 15 points for the mechanism)



(b) How would you change the reagents or the reaction conditions (i) to reduce the yield of alcohol while increasing the yield of ether and (ii) to favor elimination over substitution? (4 points)

Less alcohol, more ether?

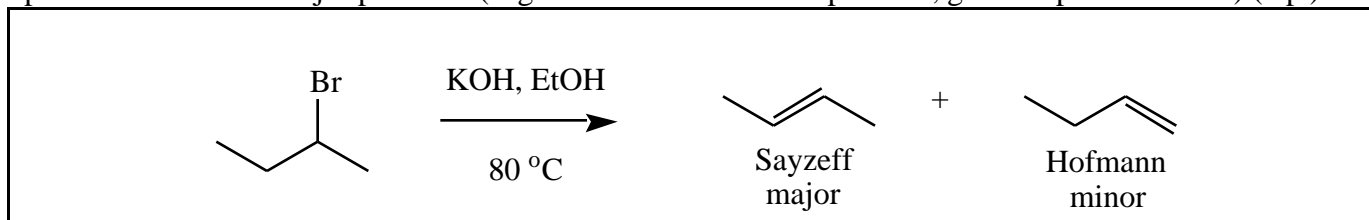
Use NaOEt instead of KOH at low T

Less substitution, more elimination?

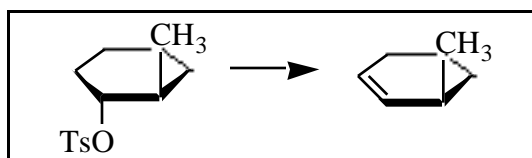
Higher T

Question 2. More on Eliminations. (26 points)

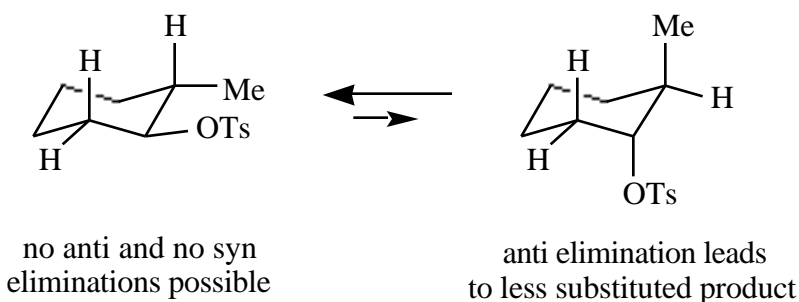
(a) Two alkenes are formed when *sec*-butyl bromide is treated with KOH in ethanol at 80 °C. Draw the structures of the alkenes, state which one is the “Sayzeff” product and which one is the “Hofmann” product. Circle the major product. (If geometrical isomers are possible, give the preferred one.) (9 p.)



(b) Treatment of *trans*-2-methylcyclohexyl tosylate with potassium *tert*-butoxide gives only 3-methylcyclohexene and the more substituted cyclohexene is not formed at all. (8 points)

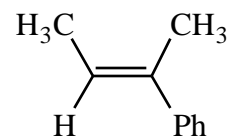


Explain this outcome considering the cyclohexane conformations.



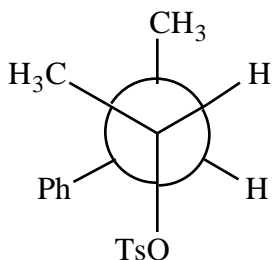
(c) One Newman projection is shown of (2*R*,3*R*)-3-phenyl-2-butyl-tosylate. Complete the Newman projections of the other two *staggered* conformations. Circle that one Newman projection with the conformation most suited for elimination and show the product expected from that elimination path. (9 points)

The product:

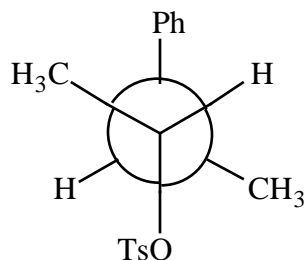


from conformation 3 (anti)

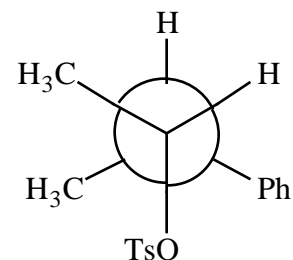
Conformation 1:



Conformation 2:

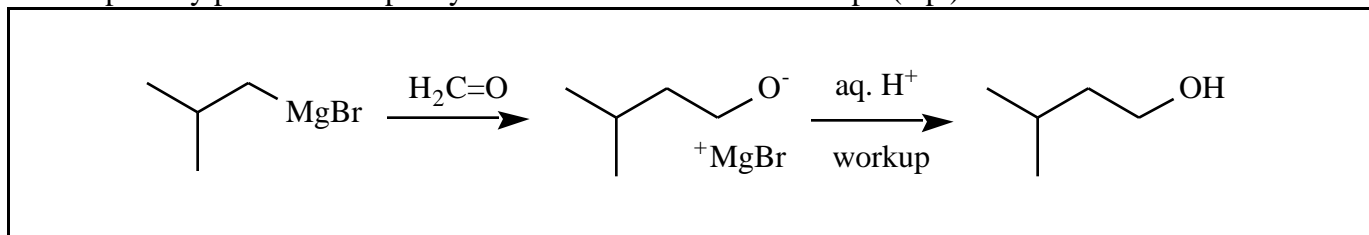


Conformation 3:

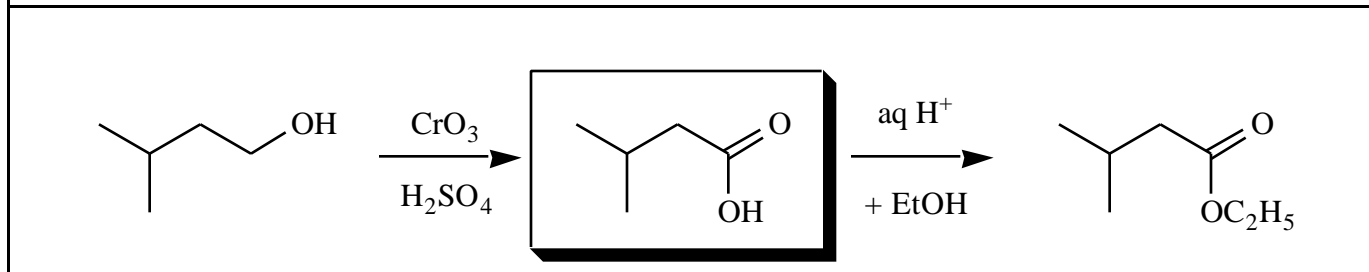
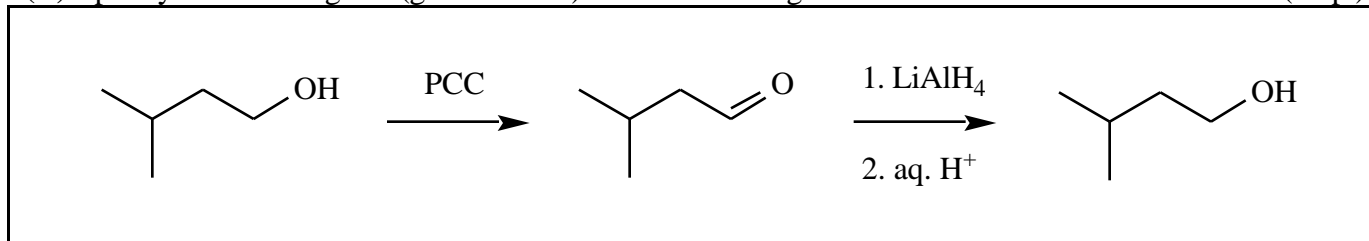


Question 3. Preparations of Alcohols and Their Reactions. (25 points)

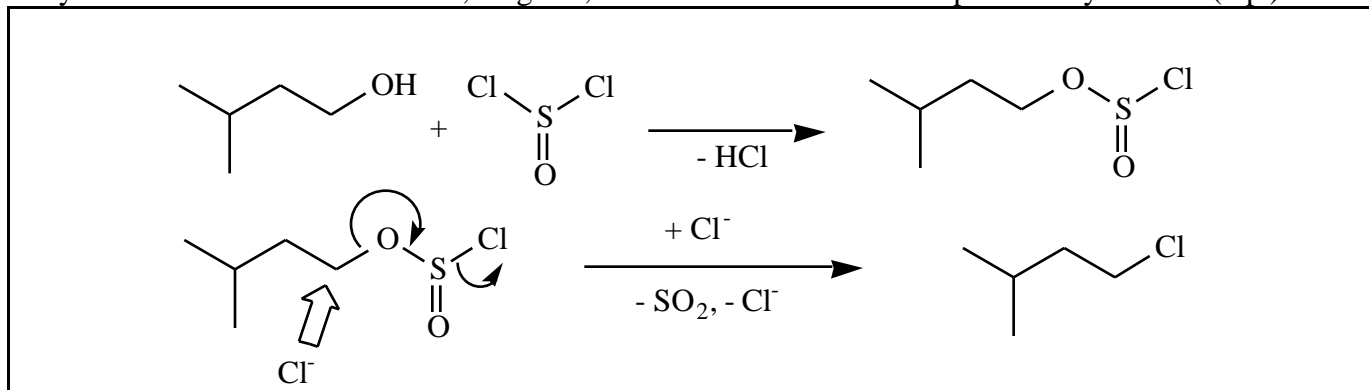
(a) A carbonyl compound is reacted with a Grignard reagent RMgBr in ether to form the alcohol shown. Specify the structures of the carbonyl compound and of the Grignard reagent needed. Draw the structure of the primary product and specify the conditions used for workup. (8 p.)



(b) Specify suitable reagents (give formula) for the following reactions and draw the intermediate. (10 p.)

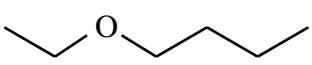


(c) The synthesis of alkylchlorides by chlorination of alkanes provides access to 2° and 3° chlorides but the yields of 1° alkylhalides usually are low. One general way to prepare primary chloroalkanes involves inorganic esters formed between 1° alcohols and **thionyl chloride**. Name the chloroalkane and suggest a synthesis for it. Draw substrates, reagents, and intermediates for all steps of the synthesis. (7 p.)

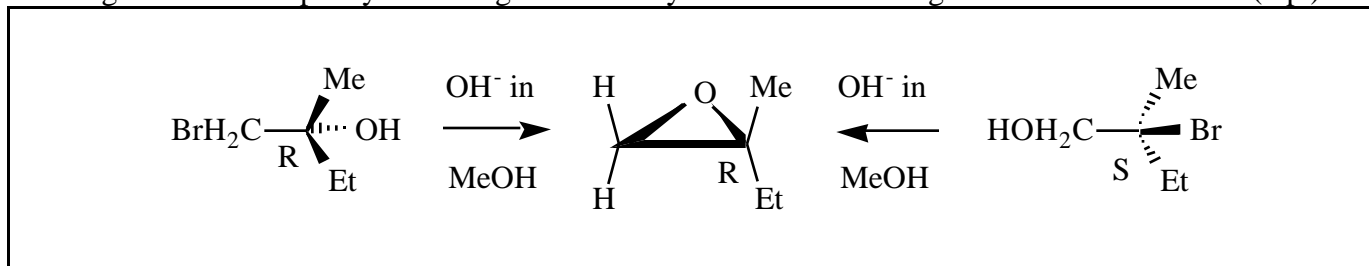


Question 4. Preparation of Ethers and Their Reactions. (24 points)

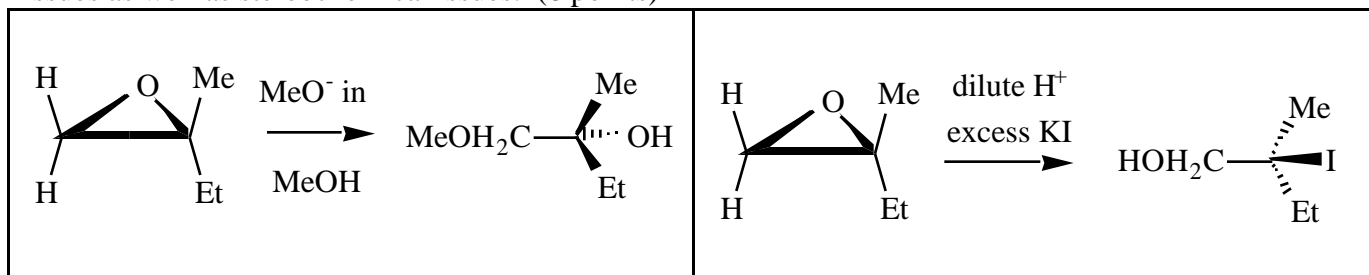
(a) The Williamson ether synthesis is a general synthesis for symmetrical and unsymmetrical ethers. The synthesis consists in a nucleophilic substitution where a _____ (2 p.) is used as the nucleophile and a _____ (2 p.) serves as the substrate. Provide the name of the ether shown and suggest two possibilities to prepare this ether via a Williamson ether synthesis. Give structures of reagents in both cases. (10 points)

	Name the ether (2 p.): butylethylether or ethoxybutane
Williamson Synthesis #1 (2 p.): Ethoxide + Br-Bu	Williamson Synthesis #2 (2 p.): Butoxide + Br-Et

(b) Specify the configuration of the asymmetric carbon in the cyclic ether using the *R/S* nomenclature. Suggest a synthesis for this ether. Draw the structure of the substrate. Indicate the stereochemistry in the starting material and specify the configuration of asymmetric atoms using the *R/S* nomenclature. (8 p.)



(c) Draw the structures of the products formed by the ether cleavages. Pay attention to regiochemical issues as well as stereochemical issues. (6 points)



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