

## Problem Set 2

Out: October 30, 1998

Due Back: November 5, 1998

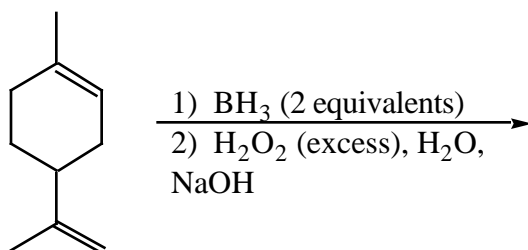
Chemistry 221, 1998

Answers to the following problems should be written, in order and labeled, on 8 1/2 x 11 inch paper. Answers written on the problem set itself will not be graded.

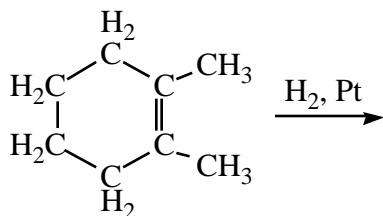
### Section A

Predict the product for the following reactions. Provide a structure which shows precise *cis/trans* relationships where appropriate. It is not necessary to show intermediates or mechanisms.

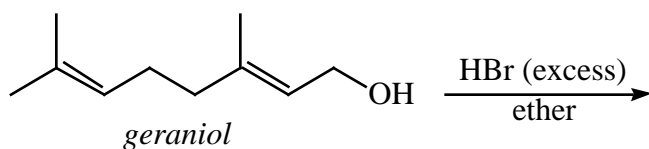
1)



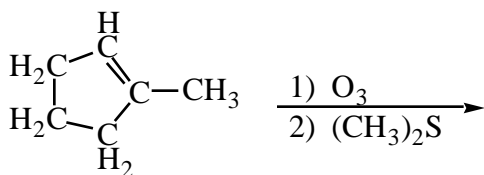
3)



2)

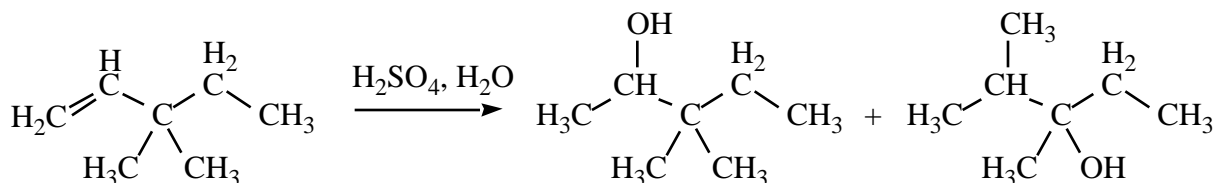


3)

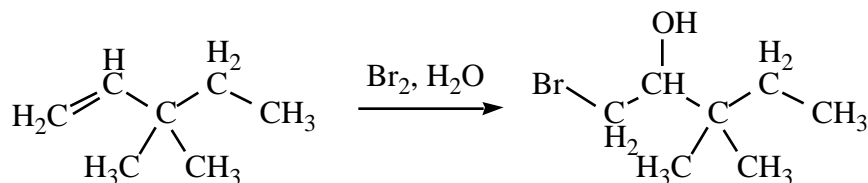


## Section B

The addition of water and sulfuric acid to 3,3-dimethyl-1-pentene gives a mixture of products, which include the following:



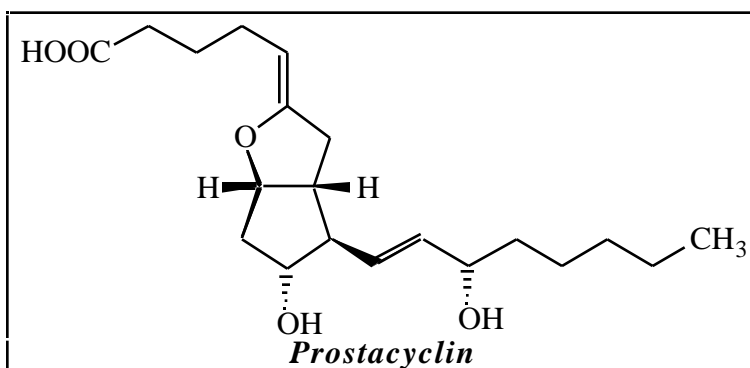
1. Provide a stepwise mechanism for the formation of both products. If the reactions have steps in common, you need only write them once (that is, if each reaction starts out the same way, write the start once, then split the mechanism at the point where they diverge).
2. If one treats the same compound with bromine in water, the reaction yields a single bromohydrin:



- Explain why this reaction provides fewer products than the one in part 1. You may wish to draw a crucial intermediate to aid your discussion; however you do not need to show the whole mechanism.

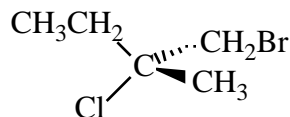
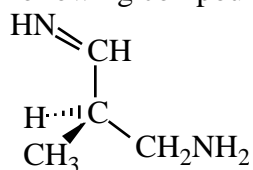
## Section C

- 1) Redraw the compound shown on the right,<sup>1</sup> circling the chiral centers. How many possible stereoisomers are there (include all possible stereoisomers)? Explain briefly how you chose how many stereoisomers there are.



<sup>1</sup>Prostacyclin. A prostaglandin produced by enzymatic transformation of prostaglandin endoperoxides (PGG<sub>2</sub>, PGH<sub>2</sub>), which dilates blood vessels and is approximately 30 times more potent than prostaglandin E1 in inhibiting platelet aggregation. PGI<sub>2</sub> is also synthesized in bovine coronary arteries as well as human arteries and veins. It has been suggested that endoperoxides released by platelets can be converted to PGI<sub>2</sub> by vascular tissue and that a balance between formation of PGI<sub>2</sub> and release of thromboxane A<sub>2</sub>, which induces platelet aggregation, controls the formation of thrombi in blood vessels. It has also been postulated that PGI<sub>2</sub> acts to stimulate platelet adenylate cyclase and to prevent the action of thrombi on phospholipid breakdown as well as platelet aggregation. [Merck Index, 12th edition]

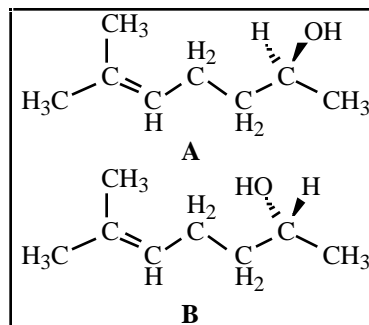
- 2) Redraw each compound shown below on your answer page. Determine configuration (R/S) for the following compounds, and show your priority assignments.



### Section D

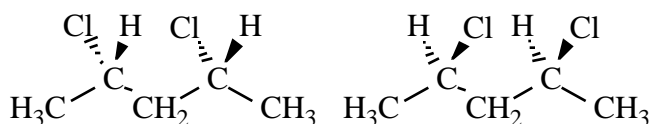
- 1) The aggregation pheromone of the ambrosia beetle<sup>1</sup> exists as a mixture of two compounds, 65% of **A** and 35% of **B**.

- Is this mixture optically active?
- Compound A has a (+) rotation. What is the sign of the rotation of compound B? ((+), (-), or can't tell)
- How can these two compounds be separated? Explain briefly.
- Assign R or S to the chiral center(s) in the molecules.

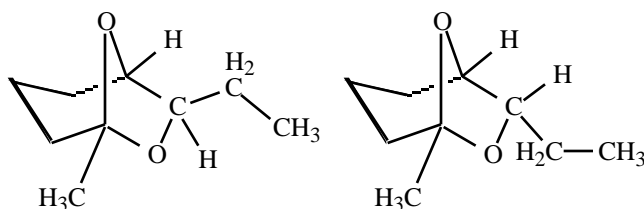


- 2) For each pair of compounds, indicate which term best indicates the kind of relationship between the compounds. The choices are: identical, enantiomer, diastereomer, constitutional isomer, not an isomer.

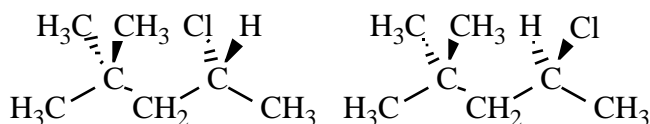
a)



b)



c)



<sup>1</sup>*Gnathotrichus sulcatus* (Scolytidae).