Problem Set 2

Out: October 30, 1998 Due Back: November 5, 1998

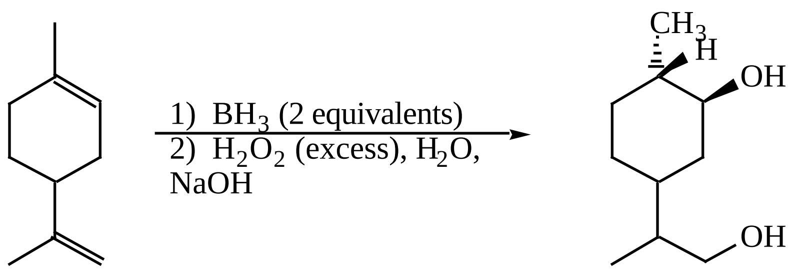
Chemistry 221, 1998

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.

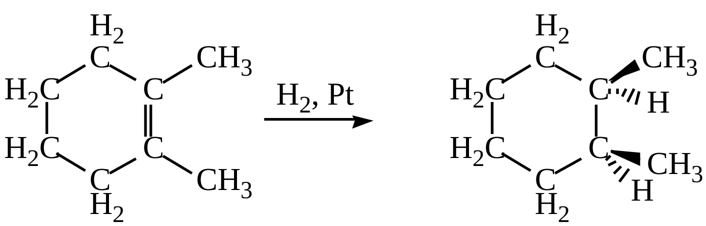
Section A

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.

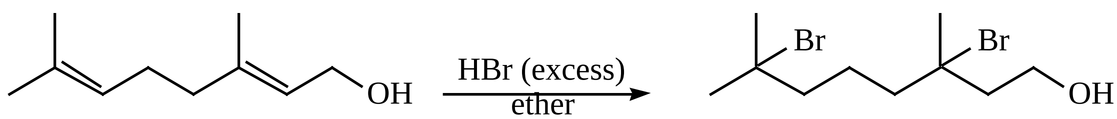
1)



3)

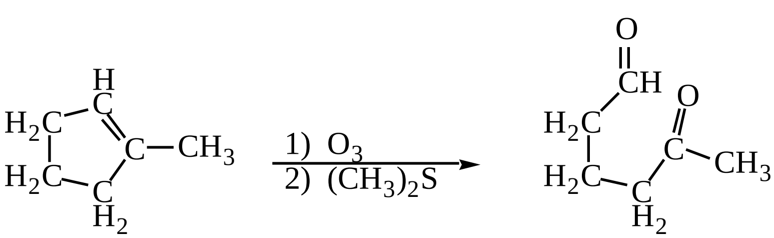


2)



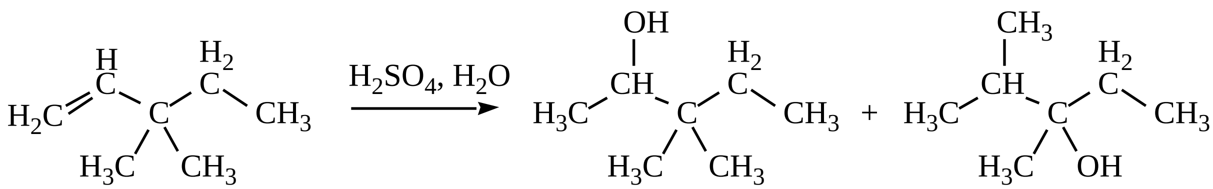
geraniol

3)

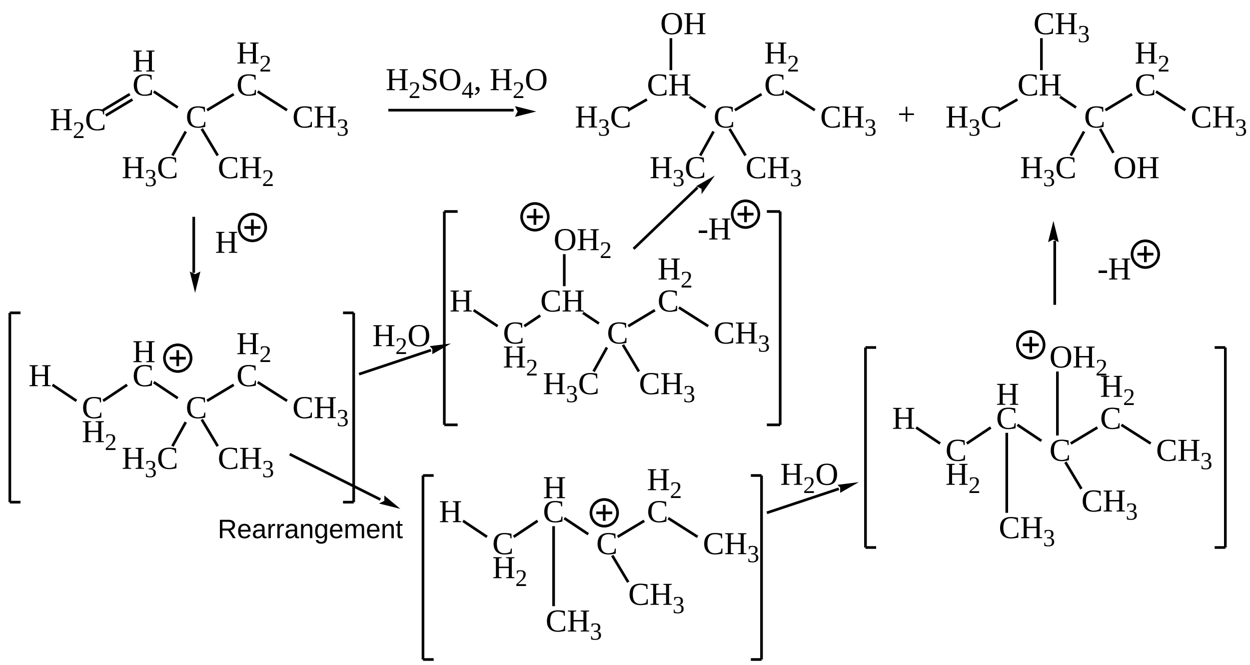


Section B

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

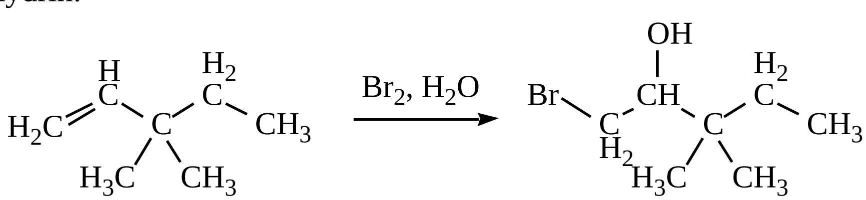


1. Provide a stepwise mechanism for the formation of both products. If the reactions have steps in common, you need only write them once (that is, if each reaction starts out the same way, write the start once, then split the mechanism at the point where they diverge).

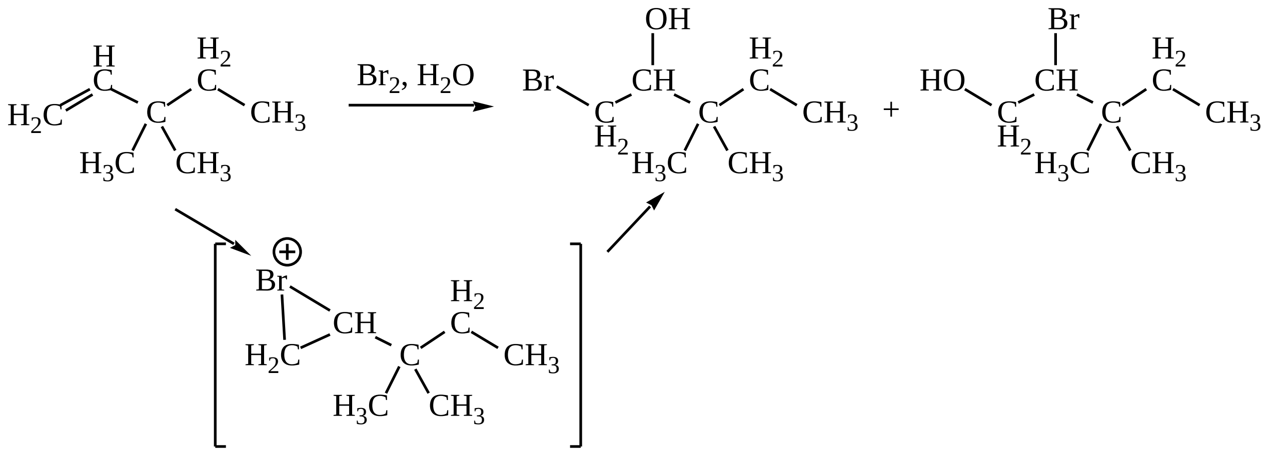


Note the split in the reaction mechanism at the first carbocation stage. If the carbocation reacts with water before it rearranges, the first alcohol will result. If it reacts after the rearrangement, the second alcohol will result. The ratio will depend on the relative rate of the two reactions.

2. If one treats the same compound with bromine in water, the reaction yields a single bromohydrin:



•Explain why this reaction is 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.

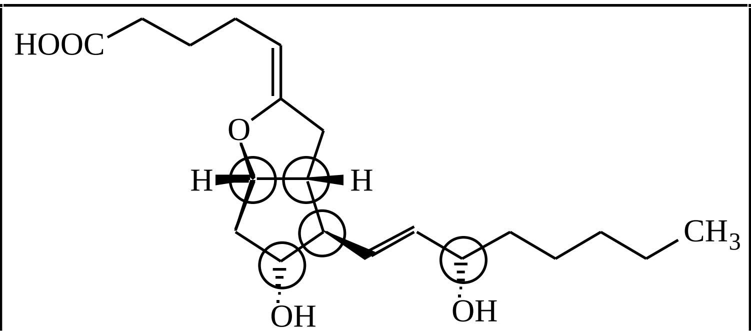


Note that the bromonium ion does not develop a full positive charge on carbon. Thus, there is insufficient driving force for rearrangement. Since rearrangement does not occur, the alcohol can only attack the leftmost two carbons.

My apologies to those who were somewhat confused by the setup: there is indeed a second product (primary OH) which was not drawn, but was alluded to in the wording of the question (it says "fewer products", not "a single product"). The figure does seem to contradict that, although it doesn't, literally.

Section C

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

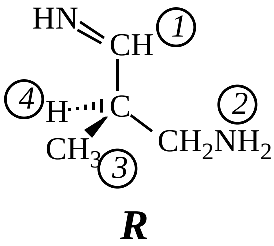


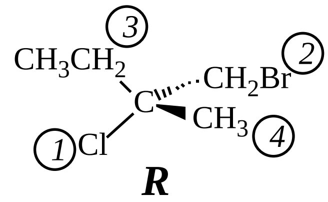
Prostacyclin

There are 128 possible stereoisomers. The 5 chiral centers make a total of 32 stereoisomers, by which we multiply by the number of *double bond* isomers (4) making a total of 128.

[1]Prostacyclin. A prostaglandin produced by enzymatic transformation of prostaglandin endoperoxides (PGG_2, PGH_2), which dilates blood vessels and is approximately 30 times more potent than prostaglandin E1 in inhibiting platelet aggregation. PGI_2 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_2 by vascular tissue and that a balance between formation of PGI_2 and release of thromboxane A2, which induces platelet aggregation, controls the formation of thrombi in blood vessels. It has also been postulated that PGI_2 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]

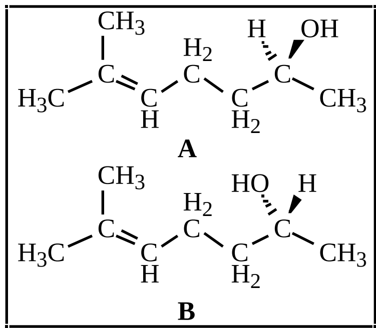
2) Redraw each compound shown below on your answer page. Determine configuration (R/S) for the following compounds, and show your priority assignments.





Section D

1) The aggregation pheremone of the ambrosia beetle[1] exists as a mixture of two compounds, 65% of **A** and 35% of **B**.



a) Is this mixture optically active?

Yes. [It is a mixture of enantiomers, but not a 50:50 one.]

b) Compound A has a (+) rotation. What is the sign of the rotation of compound B? ((+), (-), or can't tell)

It would be (-): enantiomers have opposite signs of rotation.

c) How can these two compounds be separated? Explain briefly.

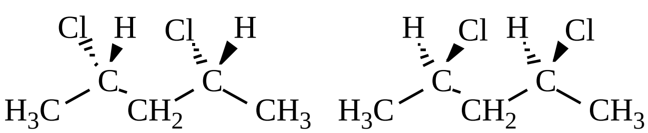
One must use chiral means. Chiral chromatography is a likely method, or making a derivative with a chiral "resolving agent". Recrystallization of the molecules shown is unlikely to be successful, since they are most likely liquids.

d) Assign R or S to the chiral center(s) in the molecules.

The chiral center in **A** is (*S*), while that in **B** is (*R*).

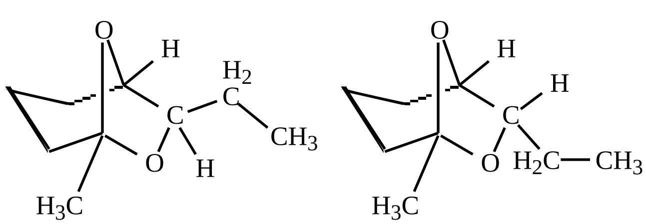
2) For each pair of compounds, indicate which term best indicates the kind of relationship between the compounds. The choices are: <u>identical</u>, <u>enantiomer</u>, <u>diastereomer</u>, <u>constitutional isomer</u>, <u>not an isomer</u>.

a)



These are identical: plane of symmetry means that "mirror images" are in fact superimposable.

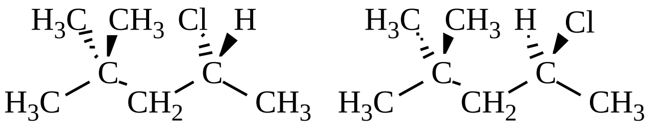
b)



Diastereomers. Only one chiral center has been modified in going from left to right. [I fixed the drawing error on your problem set: the CH_2 in the chain]

[1] *Gnathotrichus sulcatus* (Scolytidae).

c)



Enantiomers. Note that there is only one chiral center in each molecule. The methyl groups on the left are identical.