

Problem Set 2

Out: November 5, 1999 Due Back: November 12, 1999

Chemistry 221, 1999

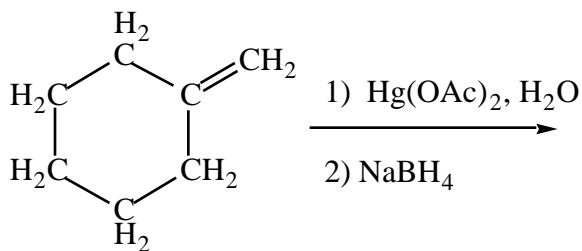
Answers to the following problems should be written, in order and labeled, on 8 1/2 x 11 inch paper. Answers written on the problem set itself will not be graded.

Questions with a bold asterisk (*) with them have 3D structures on the web. Check the problem set page for a link.

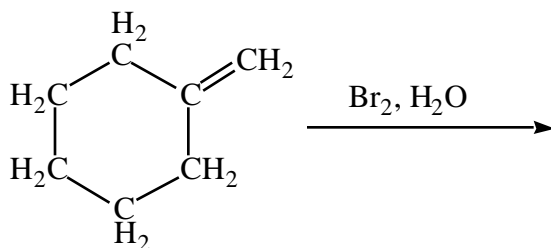
Section A

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.

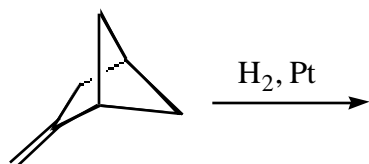
1)



2)

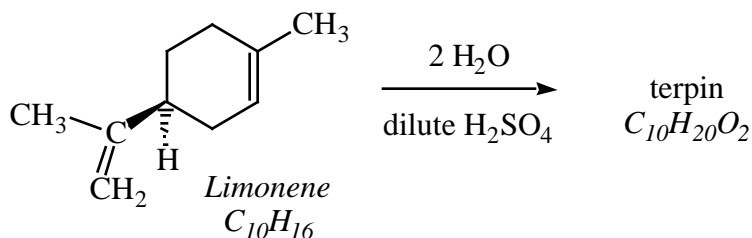


3)*



Section B

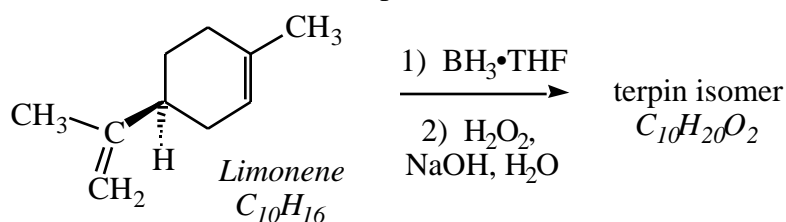
Sulfuric acid catalyzes a hydration of limonene (*) (a fragrance element found in citrus fruits) to produce "terpin." We will explore these structures further.



1) Terpin is reported to have only two isomers, one with a melting point of 104° and one with a melting point of 158° . Both isomers would be considered "major" products of

this reaction (there are other minor products). Show the structures for the two isomers of terpin. [It is not necessary to say which isomer has which mp!]

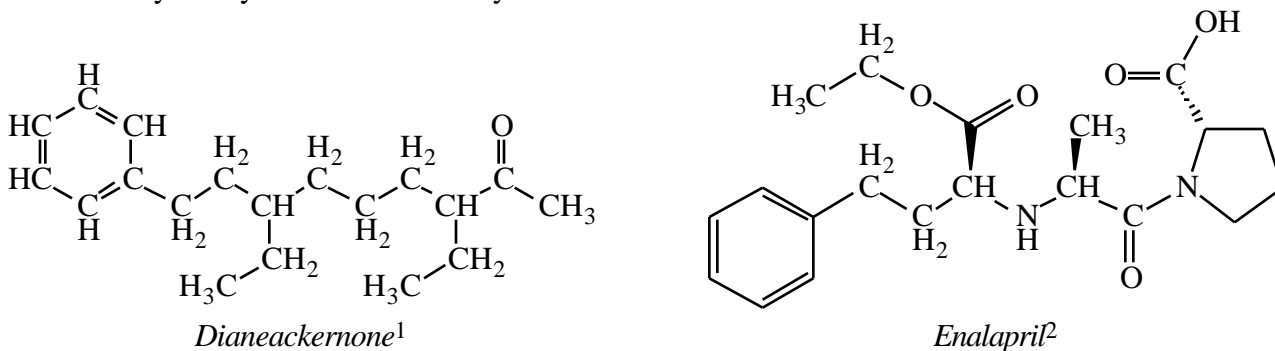
- 2) Draw the most stable chair form of each product of terpin.
- 3) Show the stepwise mechanism for the hydration of the C=C bond in the ring in limonene.
- 4) Draw the reaction energy diagram for your mechanism.
- 5) The hydroboration/oxidation of limonene shown below gives a several compounds which are constitutional isomers of terpin. Virtually no terpin is formed in this reaction. Draw a structure for the most favored product of this reaction, without specifying the stereochemical relationships.



- 6) How many stereoisomers are possible for the product you drew in the previous question?
- 7) Draw all of the stereoisomers that are likely to be formed in this reaction. Remember, each double bond could be attacked from either side.

Section C

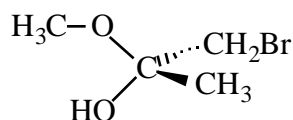
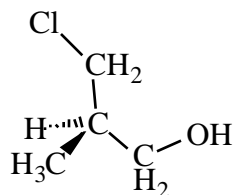
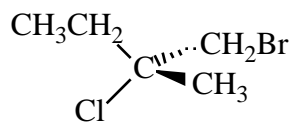
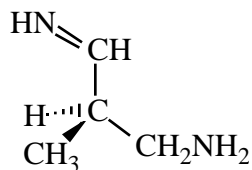
- 1)* Redraw each of the compounds shown on the below, circling the chiral centers. How many possible stereoisomers are there (include all possible stereoisomers)? Explain briefly how you chose how many stereoisomers there are.



¹ Named for the natural history author Diane Ackerman, this recently discovered compound is secreted by the skins of adult crocodiles. A crocodile pheromone, perhaps? We don't know yet. The authors of the study are making this compound available to those brave souls who study crocodile behavior. *PNAS*, **96**, 12246 and 12251 (1999).

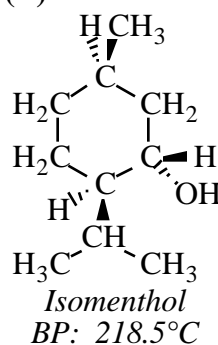
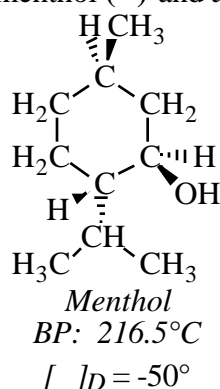
²An antihypertensive drug for humans and dogs. It acts as an angiotensin-converting enzyme (ACE) inhibitor by mimicking angiotensin I, but not allowing the cleavage reaction to proceed.

2)* Redraw each compound shown below, in any orientation you'd like, on your answer page. Determine configuration (R/S) for the following compounds, and show your priority assignments.



Section D

Show below are menthol (*) and an isomer of menthol (*)

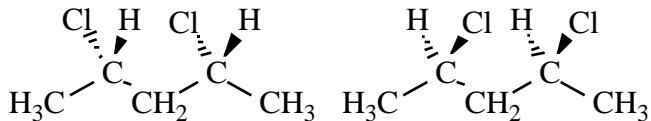


- 1) Draw the enantiomer of menthol, and give its $[\alpha]_D$ value.
- 2) How many stereoisomers of menthol are possible? Explain briefly.
- 3) What is the isomeric relationship between isomenthol and menthol?
- 4) Can you tell the $[\alpha]_D$ value of isomenthol from the information given? Why or why not?
- 5) Draw the most stable chair form of menthol and of isomenthol:
- 6) Is menthol more stable than isomenthol? Explain briefly.

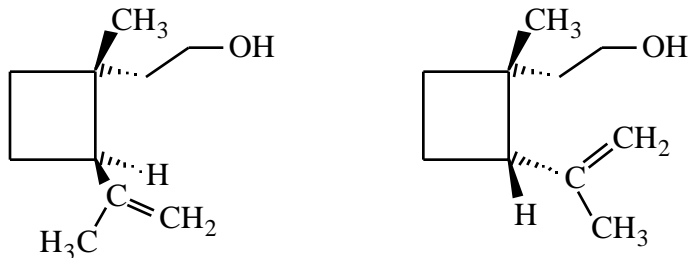
Section E

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.

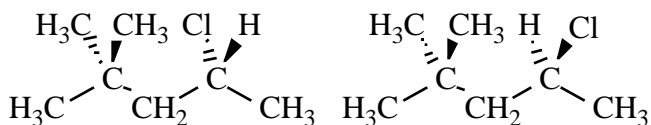
1)*



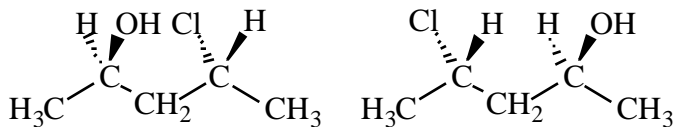
2)¹



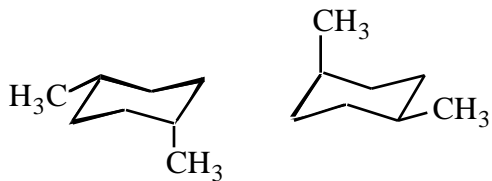
3)



4)



5)



¹Grandisol: a boll weevil sex attractants.