Department of Chemistry and Biochemistry

Chemistry 59-230/232 **Midterm #2**
Time: 50 min. **Nov. 14, 2002**

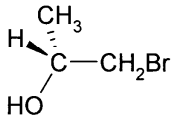
NAME _____ **ID#**_____

LAB SECTION (*enter 'no lab' if in 232 or not taking one*)_____

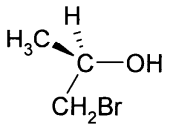
Note: ***Please answer on the test paper.*** *There is an extra sheet for rough work at the back, but it will not be marked. Tests written in pencil will be marked, but cannot be returned for remarking.*

1. Identify the relationship between each of the following pairs (i.e., enantiomers, diastereomers, identical). Are any of the compounds meso forms? If so, indicate which one(s). (total 15 marks)

a.

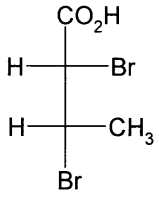


and

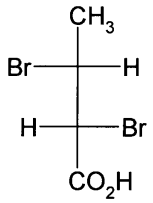


IDENTICAL

b.



and



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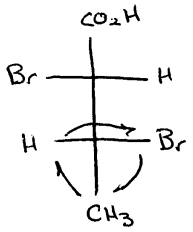

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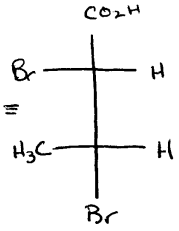
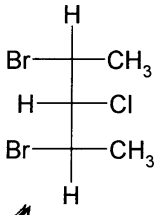
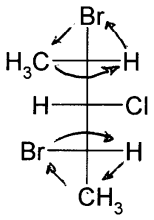


∴ ENANTIOMERS

c.



and



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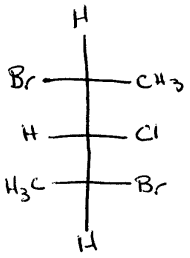
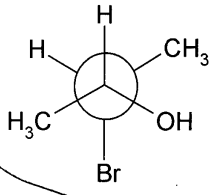
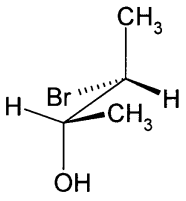


∴ DIASTEREOMERS

d.



and



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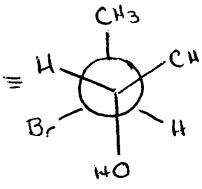

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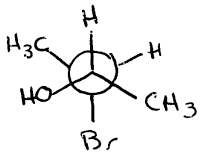
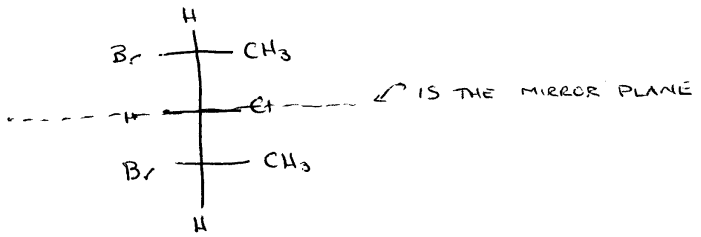


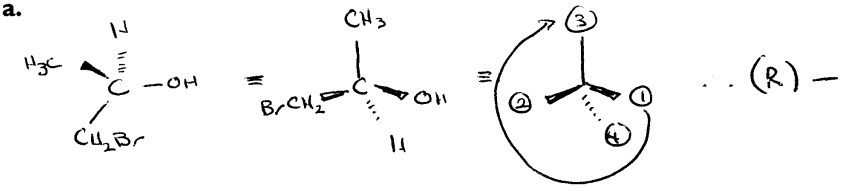
∴ ENANTIOMERS.

THIS IS A MESO COMPOUND

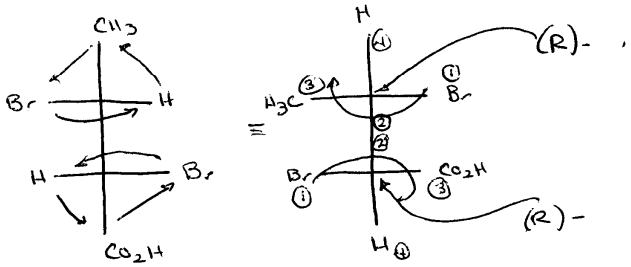


2. For the structures on the **right** side 1a and 1b only, identify each chiral centre as (R)- or (S)-. Show how you arrived at your answer (5 marks each, total 15)

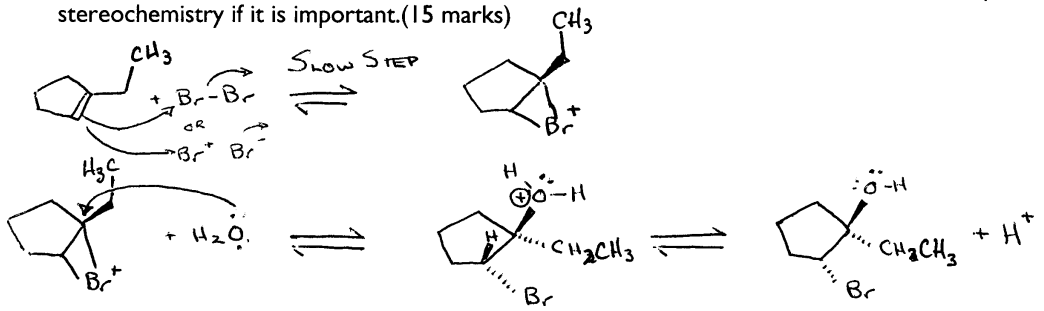
a.



b.

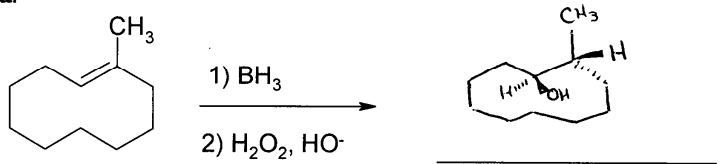


3. Draw the complete mechanism of the reaction of bromine in water (solvent) with 1-ethylcyclopentene. Indicate whether each step is reversible or irreversible, and which is the slow step. Show any stereochemistry if it is important.(15 marks)



4. For each of the following reactions, fill in the blank with the structural formula of the required chemical. Show any required catalysts over the reaction arrow. Be sure to include stereochemistry where it is important. (Total 25 marks)

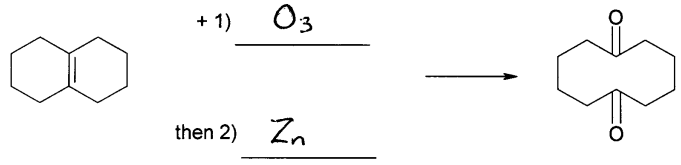
a.



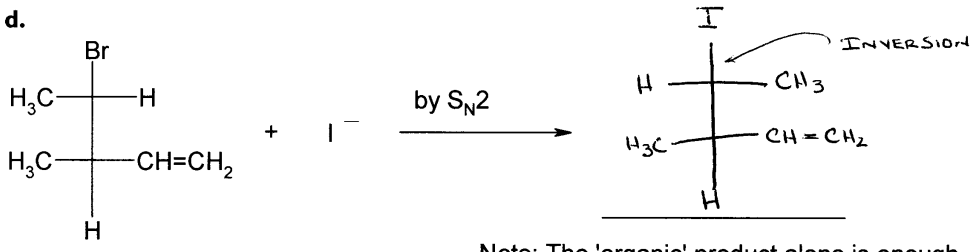
there is not a mistake in the structure

b.

c.

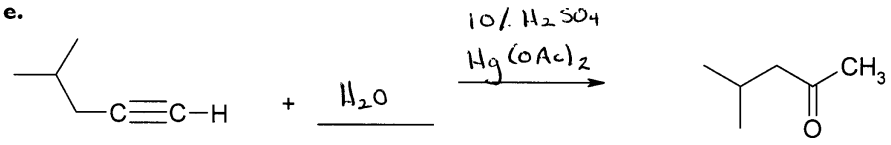


d.



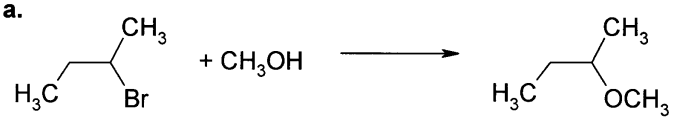
Note: The 'organic' product alone is enough

e.

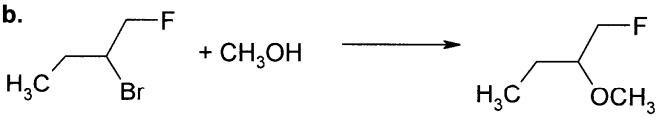


5. Rank the following in terms of tendency to undergo S_N1 substitution (as opposed to S_N2) . Give reasons for you ordering. You may use drawings to indicate your reasoning if it makes your answer clearer, and would I would suggest it in at least one case. (15 marks)

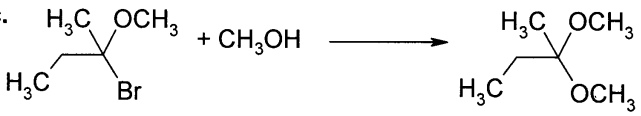
a.



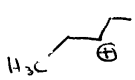
b.



c.

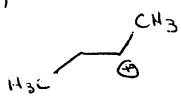


b) LEAST S_N1, MOST S_N2



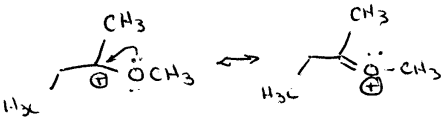
IS 2°, DESTABILIZED BY -I FLUORINE SUBSTITUENT

a) INTERMEDIATE CASE



IS 2° NOT ANY PARTICULARLY STRONG ADDITIONAL STABILIZING OR DESTABILIZING GROUPS

c) MOST S_N1, LEAST S_N2



IT'S ARGUABLE WHETHER YOU'D CALL THIS 2° OR 3° (I'D USE 3°), BUT THERE'S AN ADDITIONAL METHOXY GROUP STABILIZING THE ⊕ CHARGE BY RESONANCE (SHOWN)

d. Assuming that each starting material from above is optically active, which of the three is most likely to give an optically active product? (3 of the 15 marks)

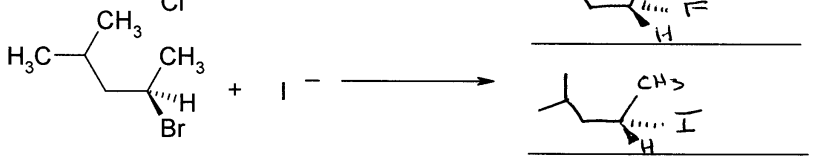
b) IS. SINCE IT HAS THE MOST S_N2 CHARACTER, IT HAS THE MOST LIKELYHOOD TO GO WITH INVERSION

6. Rank the following as to which reaction is fastest to which is slowest. <u>All are going by S_N2</u> . Include the products, indicating the stereochemistry if important. (15 marks)

a.

b.

c.



C. IS THE FASTEST BY S_N2, AS Br^- IS > Cl^- AS LEAVING GROUP, AND I^- > F^- AS NUCLEOPHILE. THEREFORE C. HAS THE BETTER NUCLEOPHILE AND BETTER LEAVING GROUP.

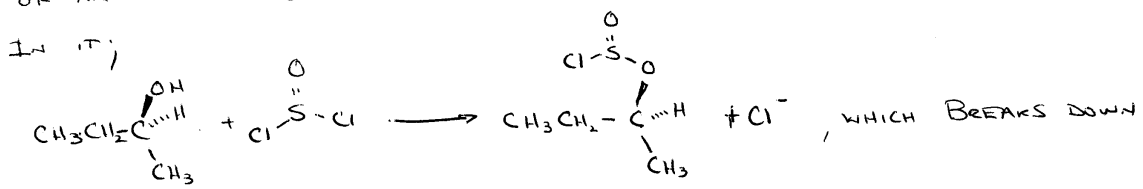
a. IS THE INTERMEDIATE CASE, AS IT HAS THE BETTER NUCLEOPHILE (I^-) BUT THE LESS GOOD (ALTHOUGH STILL QUITE GOOD) LEAVING GROUP (Cl^-)

b. IS THE SLOWEST BY S_N2, AS IT HAS THE POORER NUCLEOPHILE (F^-) AND THE LESS GOOD LEAVING GROUP (Cl^-)

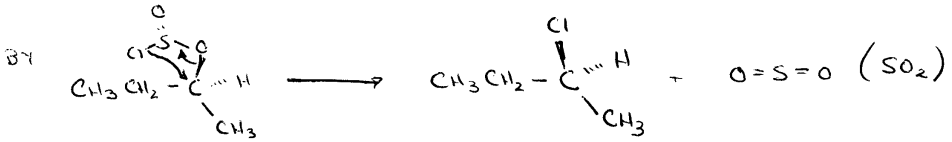
Bonus. Here's your chance to be creative. In nucleophilic substitution reactions, the stereochemical outcome we have *not* seen is retention of configuration, yet there are some less common cases where this can be made to happen reliably. Design such a reaction (that would give nucleophilic substitution with *retention* of configuration at a <u>single</u> chiral centre). You may use any substrate and any nucleophile you deem fit, at long as they makes bonding sense. (Up to 5 additional marks)

WELL, THERE ARE SEVERAL, BUT ONE OF THE MOST COMMON IS THE CONVERSION OF AN ALCOHOL TO AN ALKYL CHLORIDE BY THIONYL CHLORIDE ($SOCl_2$)

IN IT;



BY



SINCE THE ULTIMATE SUBSTITUTION GROUP IS 'TIED' TO THE LEAVING GROUP, IT HAS TO COME IN ON THE SAME SIDE FROM WHICH THE LEAVING GROUP DEPARTED --- HENCE RETENTION

THIS MECHANISM HAS A NAME, TOO; IT'S S_Ni (FOR INTERNAL)