

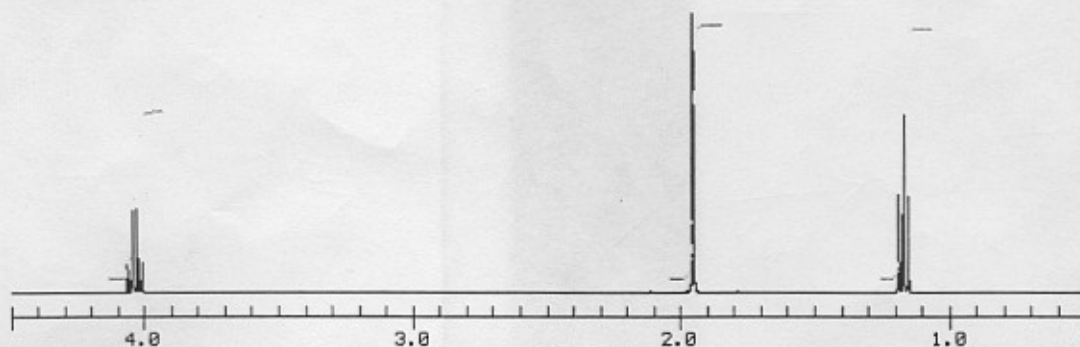
Chemistry 210 -- EXAM 3 (Fall 2003 - Dr. Robertson)

***** BEFORE BEGINNING EXAM, PLEASE READ THE FOLLOWING *****

The exam consists of this cover sheet, which contains an extra credit problem, which is optional. There are 13 problems to solve. The time limit for this exam is 2 hours. Please read problems carefully so that you understand the entire problem. *No work = no credit.*

Signed _____

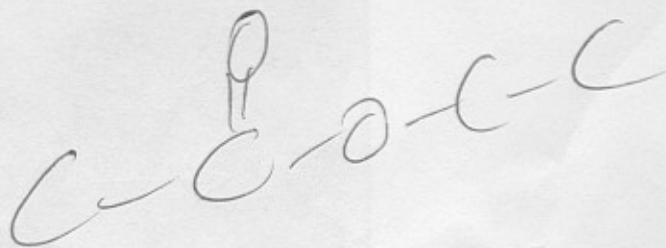
OPTIONAL EXTRA CREDIT (3 points):



Use the NMR spectrum above to answer this question. The formula for this compound is $C_4H_8O_2$. What is a plausible structure for this compound? It will be either an acid, an alcohol or an ester.

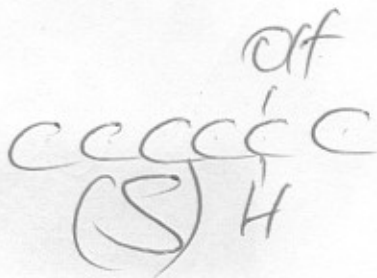
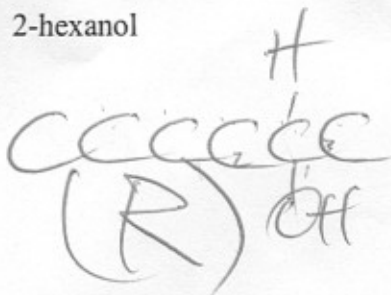
How many types of Hydrogens are present? 3 (1 point)

What is a possible structure for this compound (show structure below)? (2 points)



9 1. (i) Draw both enantiomers (if any exist) for the following compounds (1 point each). (ii) Then give the *R* or *S* designation for each (1 point).

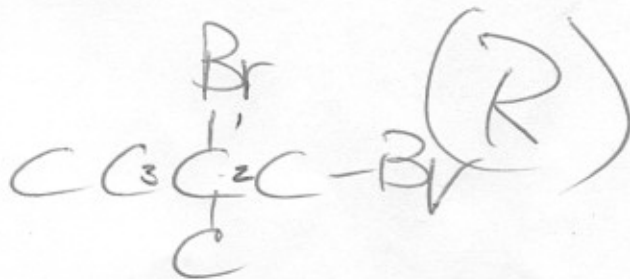
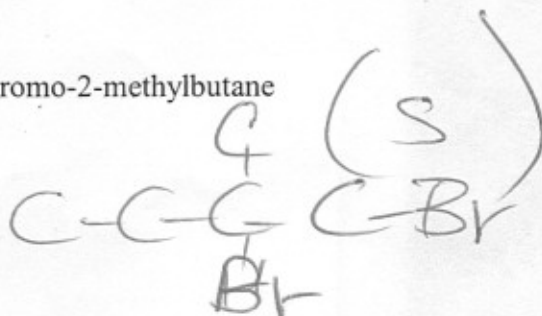
2-hexanol



2-chloro-2-methylbutane

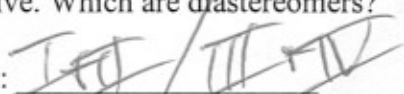
NONE

1,2-dibromo-2-methylbutane

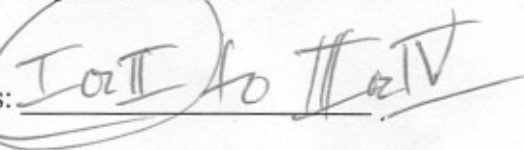


8 2. Draw stereochemical formulas for the four possible stereoisomers of 2,3-dibromopentane (label them I, II, III, and IV and use list these numbers in the space provided). Label pairs of enantiomers. Which are optically active. Which are diastereomers?

Enantiomers:

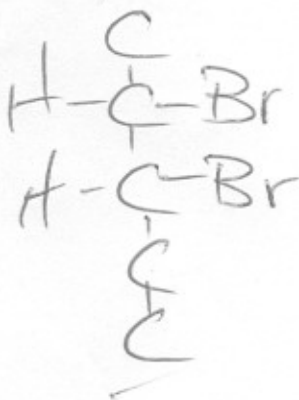


Diastereomers:

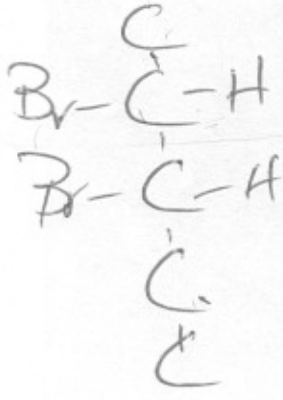


Optically Active:

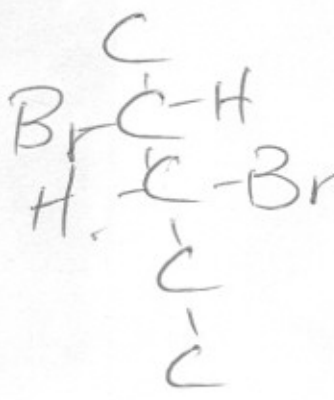
all



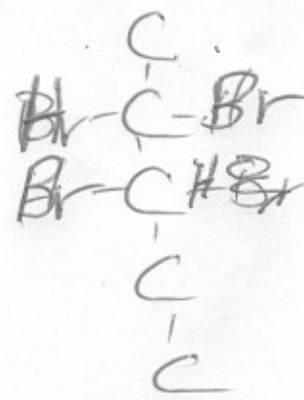
I



II

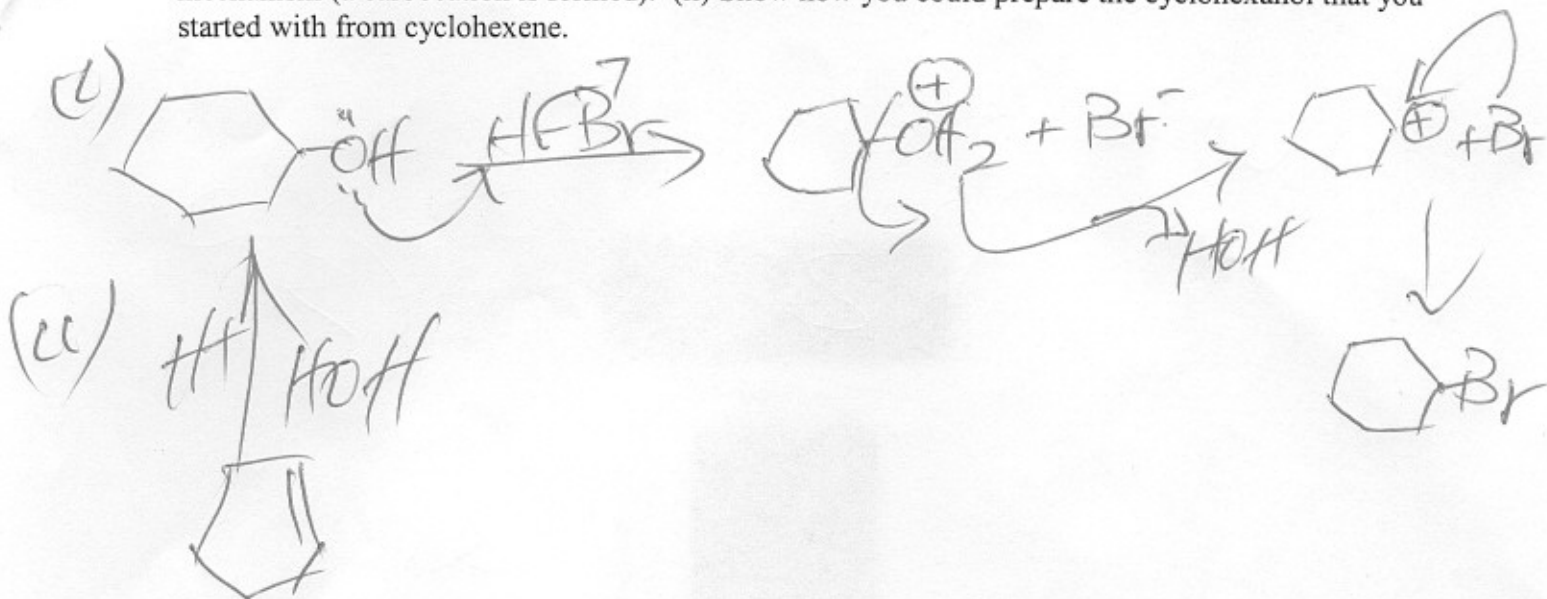


III

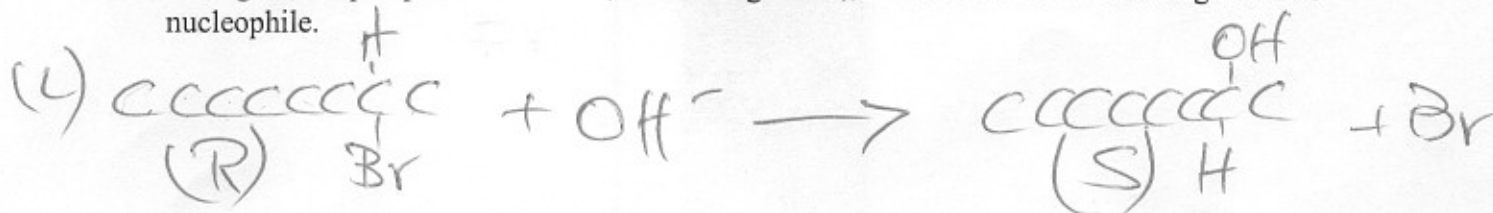


IV

- 8 3. You desire to convert cyclohexanol into bromocyclohexane. (i) Show all reagents and the reaction mechanism (with arrows!) by which this transformation could occur, using the S_N1 reaction mechanism (a carbocation is formed). (ii) Show how you could prepare the cyclohexanol that you started with from cyclohexene.



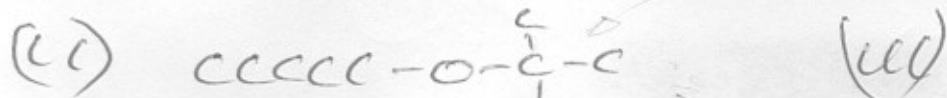
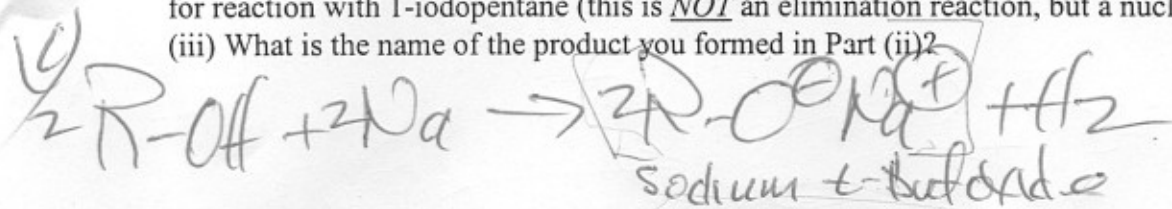
- 12 4. You start with pure $R(-)$ -2-bromooctane and react it with the hydroxide ion (OH^-). Your desired product is $S(+)$ -2-octanol, which, as it turns out, is your only product. (i) Draw the correct stereoisomeric structures for the reactant and product. (ii) Then, tell how you know which reaction pathway (S_N1 or S_N2) was followed to give 100% pure product. (iii) If you react with water (in ethanol) instead, you produce a mixture of 83% $S(+)$ -2-octanol and 17% $R(-)$ -2-octanol. Account for having an unequal product mixture, even though an S_N1 reaction is followed using water as nucleophile.



(ii) total inversion is S_N2

(iii) some carbocation formed but not all reaction was S_N1

- 6 5. (i) Show a balanced equation for the reaction between metallic Na with t-butyl alcohol. Give product names. (ii) Using the base (nucleophile) you just produced in this reaction predict the major product for reaction with 1-iodopentane (this is NOT an elimination reaction, but a nucleophilic substitution). (iii) What is the name of the product you formed in Part (ii)?



(iii) t-Butyl pentyl ether

- 6 6. The concentration of naphthalene dissolved in chloroform is 9.15 g per 100 mL. In a 50-cm polarimeter, an optical rotation of -22.2° is observed (α). (i) Calculate the specific rotation ($[\alpha]$) of naphthalene using the formula shown. (ii) Predict the observed rotation if the concentration of naphthalene were 4.575 g per 100 mL of the solution, and if a 25-cm polarimeter were used. [length (dm) = l ; solute concentration (g per 100 mL) = d]

$$[\alpha] = \frac{\alpha \times 100}{l \times d}$$

- 10 7. Define each of the following:

optical activity:

rotation of plane polarized light

levorotatory:

rotate to the left
negative

diastereomer:

not enantiomers but related to another set of enantiomers

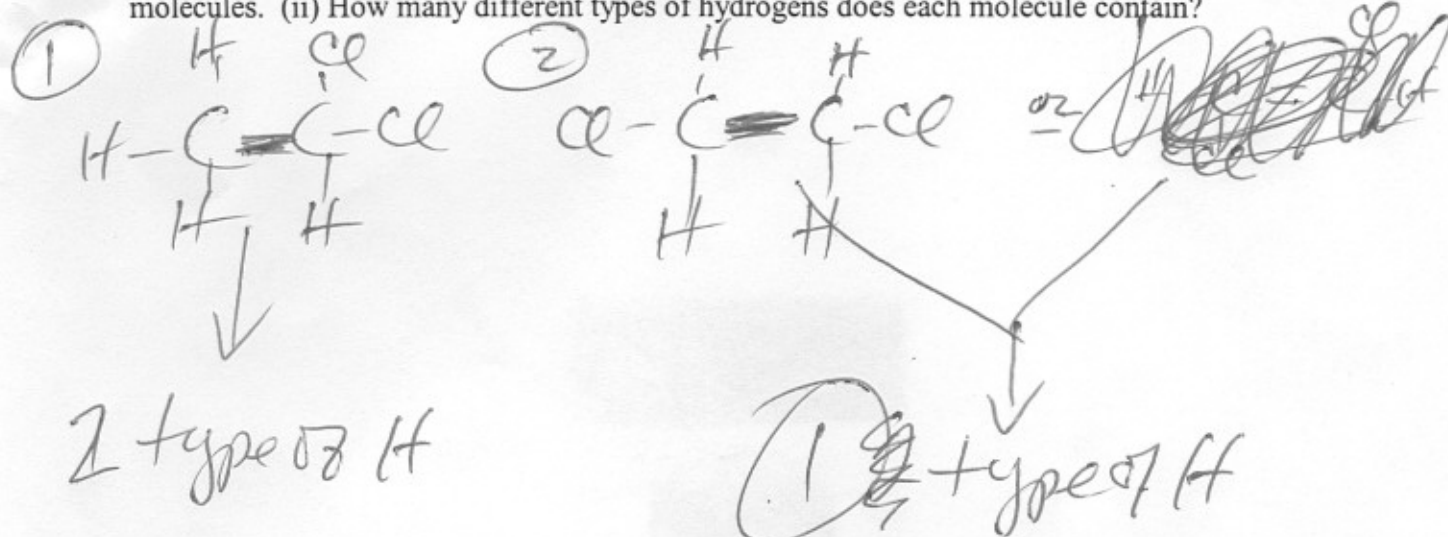
nucleophile:

Lewis base

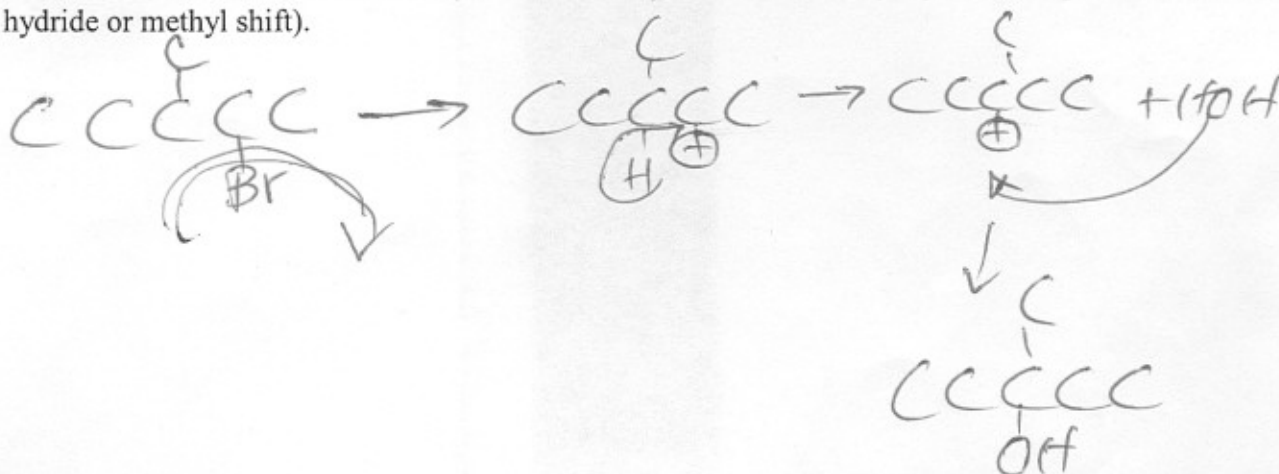
electrophile:

Lewis acid

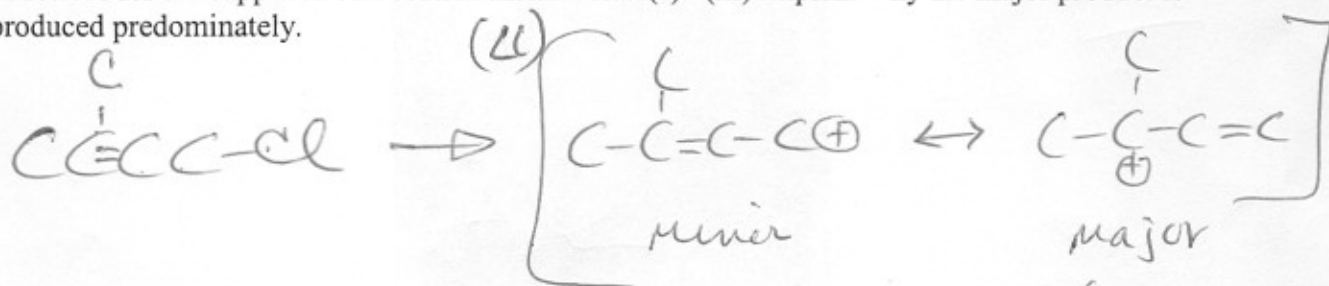
- 6 8. There are two molecules having molecular formulas of $C_2H_4Cl_2$. (i) Show structures for these molecules. (ii) How many different types of hydrogens does each molecule contain?



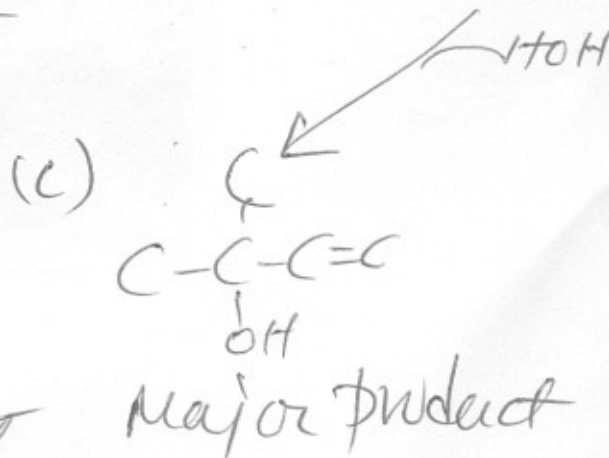
- 6 9. When 2-bromo-3-methylpentane reacts in water, the major product (93%) is 3-methyl-3-pentanol. Show the S_N1 reaction mechanism (via carbocation), and how the major product is produced (think: hydride or methyl shift).



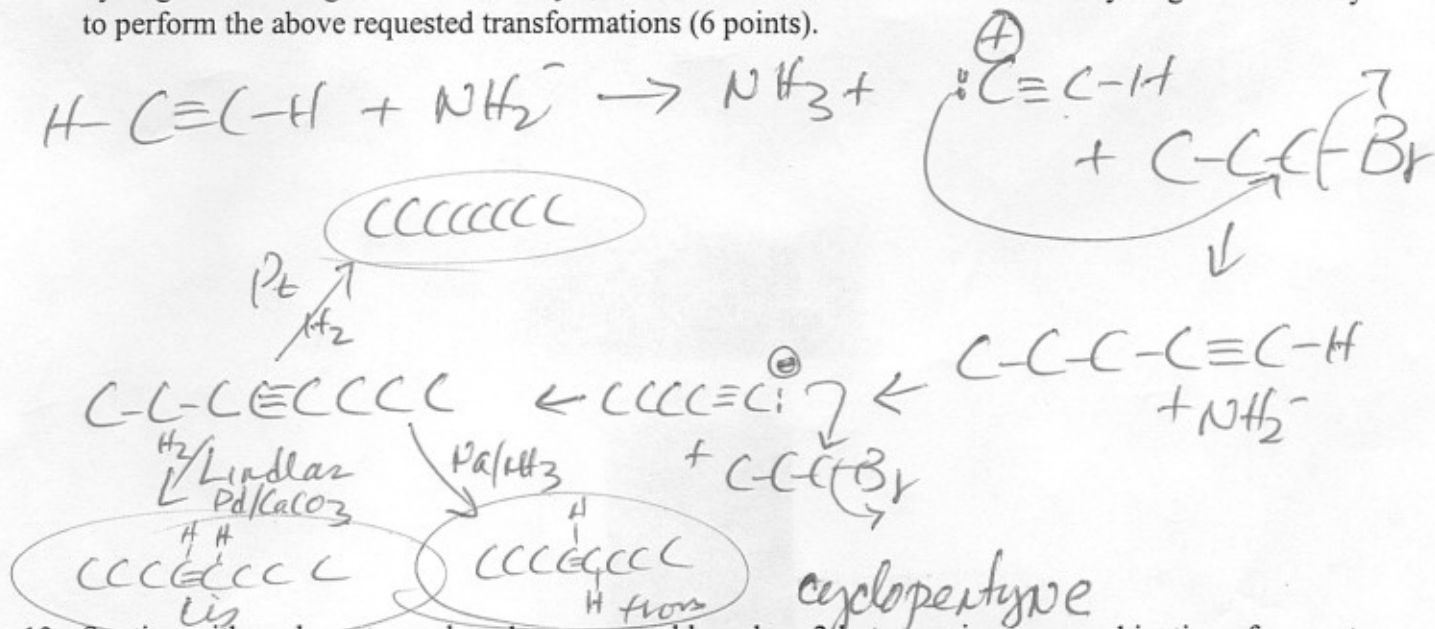
- 8 10. Thinking about how a double bond affects the rest of the molecule, (i) show the major alcohol product when 1-chloro-3-methyl-2-butene reacts with water in acid (H^+). (ii) Draw the possible resonance structures for the supposed carbocation intermediate(s). (iii) Explain why the major product is produced predominately.



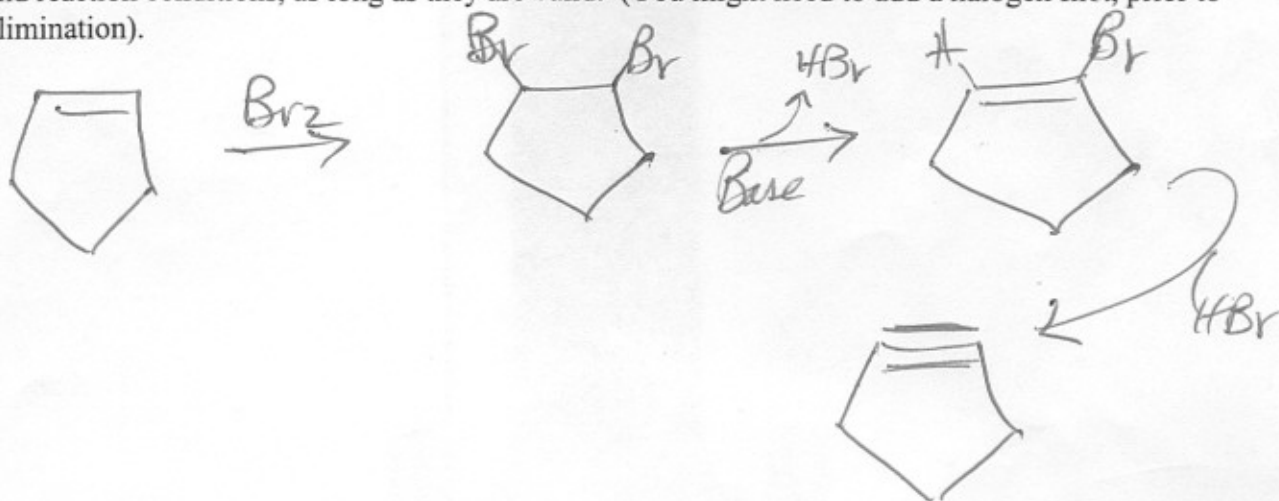
(ii) resonance favors (+) charge on 3° carbon after allylic rearrangement



- 10 11. (i) Starting with acetylene (ethyne) and the appropriate alkyl bromide(s), show how you could produce 4-octyne (4 points). (ii) Show the products for reaction of 4-octyne with catalytic hydrogenation, hydrogenation using the Lindlar catalyst, and Na with ammonia. You can use any reagents necessary to perform the above requested transformations (6 points).



- 5 12. Starting with cyclopentene, show how you could produce 2-butyne using any combination of reagents and reaction conditions, as long as they are valid. (You might need to add a halogen first, prior to elimination).



- 6 13. (i) Starting with 3-chloro-3-methylcyclohexene, show the reaction pathway and possible products (two of which can be formed, for reaction with water (think allylic!)). (ii) Show the possible resonance structures for this reaction. (iii) Explain why this is the preferred product.

