

FINAL EXAMINATION
Chemistry 3A

Key

Name: _____

SID #: _____

Print first name before second!

Use capital letters!

GSI (if you are taking Chem 3AL): _____

Peter Vollhardt

May 11, 2016

Please provide the following information if applicable.

Making up an I Grade _____

If you are, please indicate the semester during which you took previous Chem 3A and the instructor:

Semester

Instructor

Auditor _____

Please write the answer you wish to be graded in the boxed spaces provided.

Do scratch work on the back of the pages. This test should have **23** numbered pages. Check to make sure that you have received a complete exam. A good piece of advice: **Read carefully over the questions (at least twice); make sure that you understand exactly what is being asked; avoid sloppy structures or phrases. It is better to be pedantic in accuracy now than sorry later! Good Luck!**

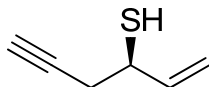
You will not really need it, but here is a partial periodic table.

Period							Halogens	Noble gases
First	H ¹							He ²
Second	Li ^{2,1}	Be ^{2,2}	B ^{2,3}	C ^{2,4}	N ^{2,5}	O ^{2,6}	F ^{2,7}	Ne ^{2,8}
Third	Na ^{2,8,1}	Mg ^{2,8,2}	Al ^{2,8,3}	Si ^{2,8,4}	P ^{2,8,5}	S ^{2,8,6}	Cl ^{2,8,7}	Ar ^{2,8,8}
Fourth	K ^{2,8,8,1}						Br ^{2,8,18,7}	Kr ^{2,8,18,8}
Fifth							I ^{2,8,18,18,7}	Xe ^{2,8,18,18,8}

Note: The superscripts indicate the number of electrons in each principal shell of the atom.

- I. [48 Points] Provide the IUPAC name or draw the structure, as appropriate, of the following molecules. Remember the priority of functional groups in choosing names, indicate the correct stereochemistry (e.g. *R*, *S*, *cis*, *trans*, and *E*, *Z*), and do not forget about the alphabetical ordering of substituents!

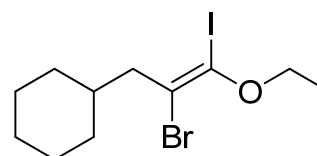
a.



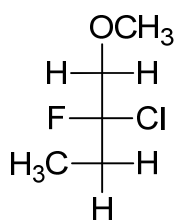
(*R*)-1-Hexen-5-yne-3-thiol

b.

(*E*)-(2-Bromo-3-ethoxy-3-iodo-2-propenyl)cyclohexane

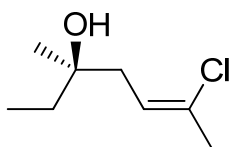


c.



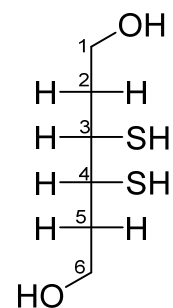
(*R*)-2-Chloro-2-fluoro-1-methoxybutane

d.

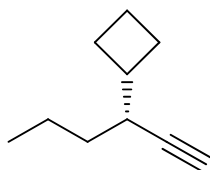


(*R,Z*)-6-Chloro-3-methylhept-5-en-3-ol

e.

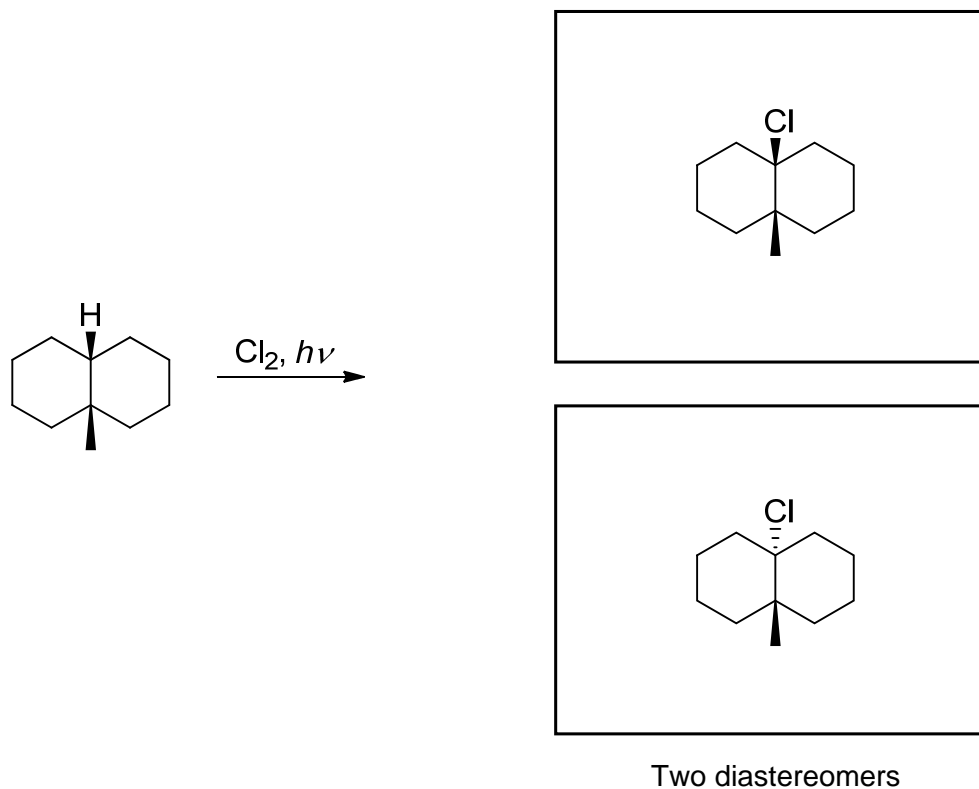
meso-3,4-Dimercapto-1,6-hexanediol

f.

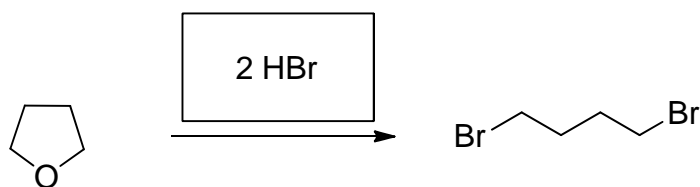
*(R)*-3-Cyclobutyl-1-hexyne

II. [135 Points] Add the missing starting materials, reagents, or products (aqueous work-up is assumed where necessary). Don't forget **stereochemistry**! Complete the stencils, when provided. **Note:** In the reagent boxes above the arrows, enter one step only. Multistep sequences are clearly indicated by several boxes labelled "1., 2., 3.," etc.

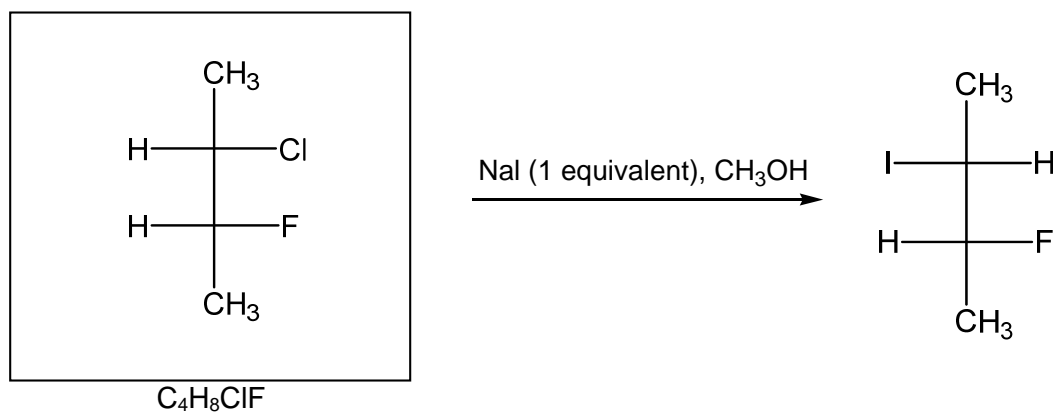
a.



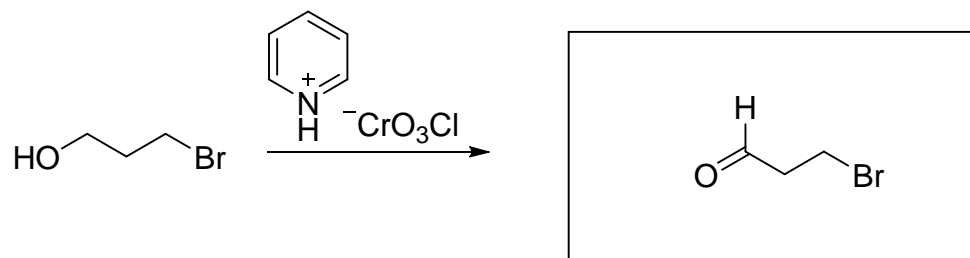
b.



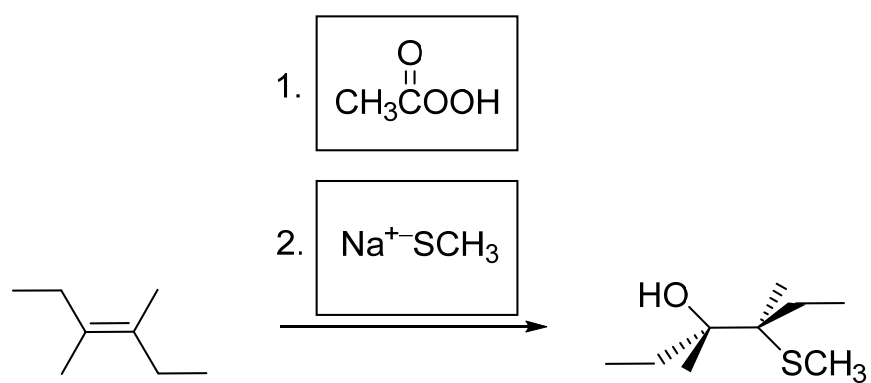
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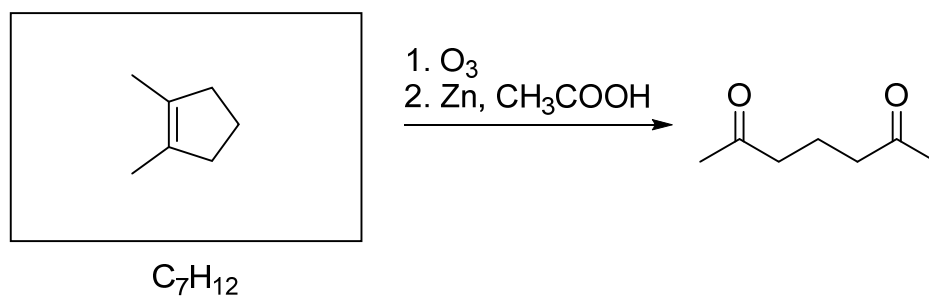
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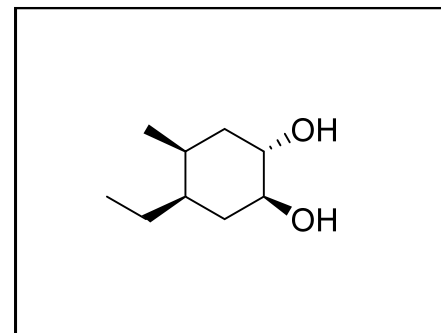
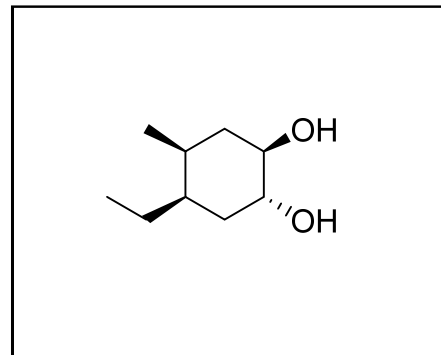
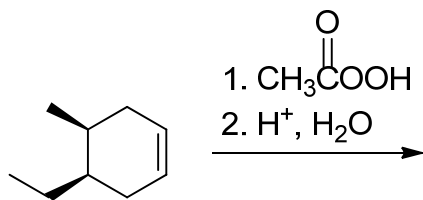
e.



f.

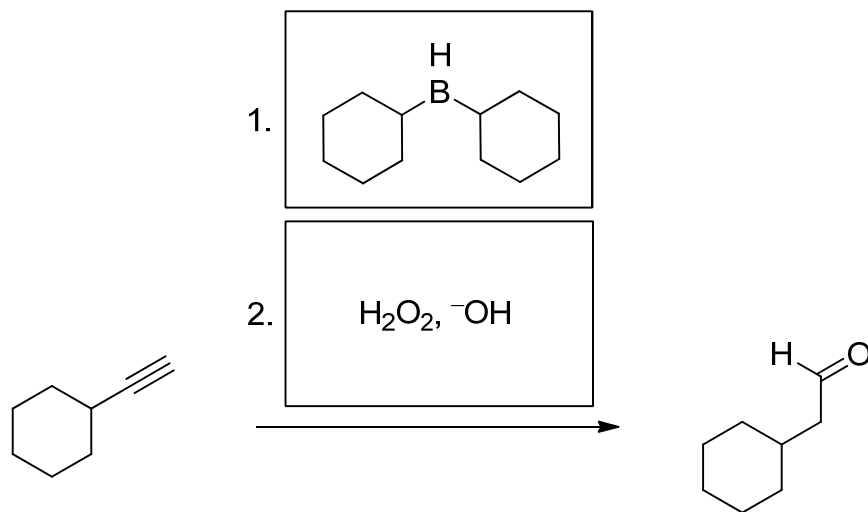


g.

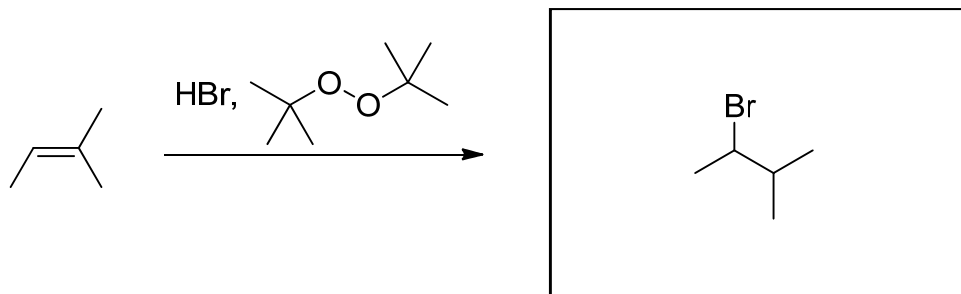


Two diastereomers

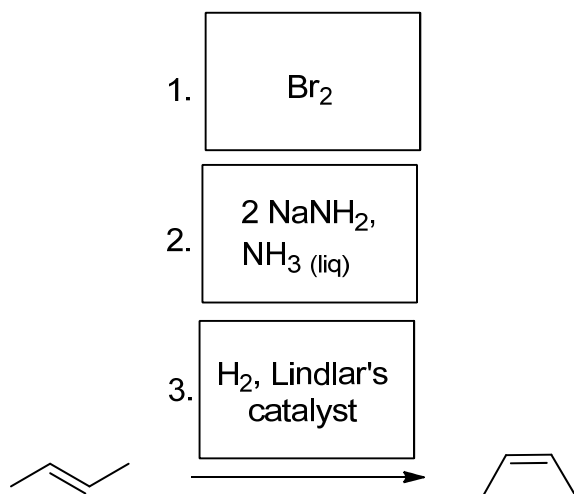
h.



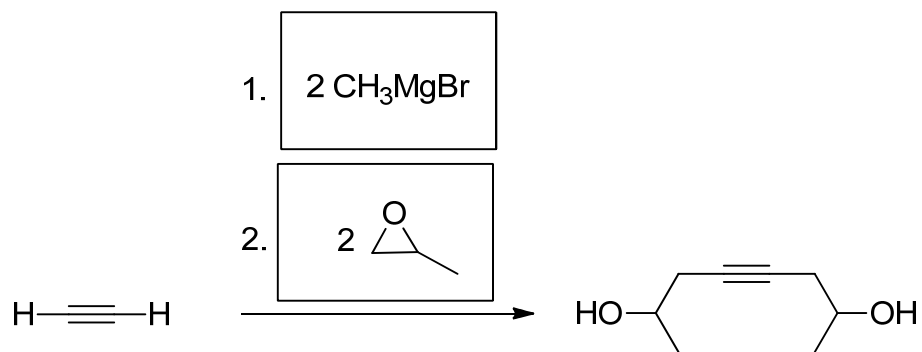
i.



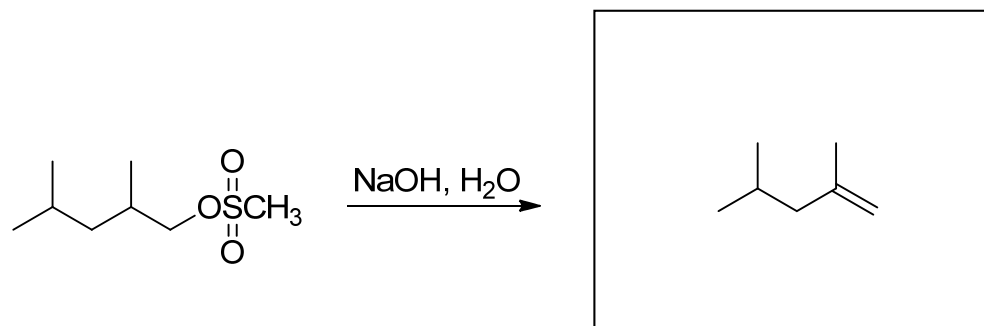
j.



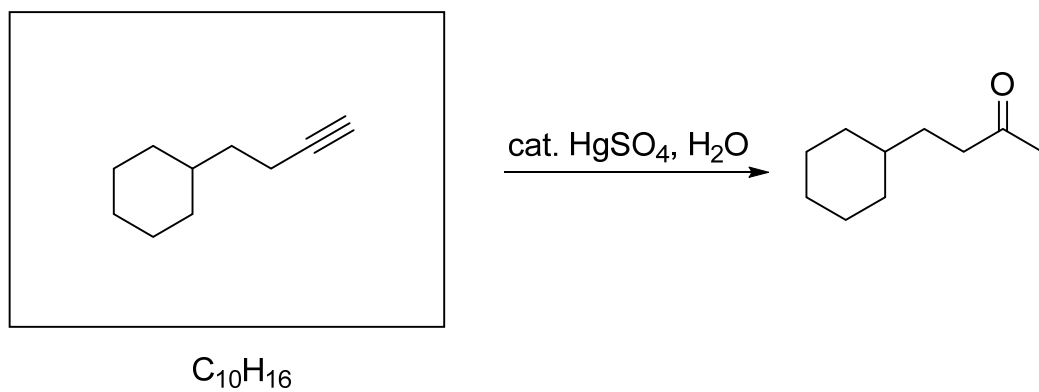
k.



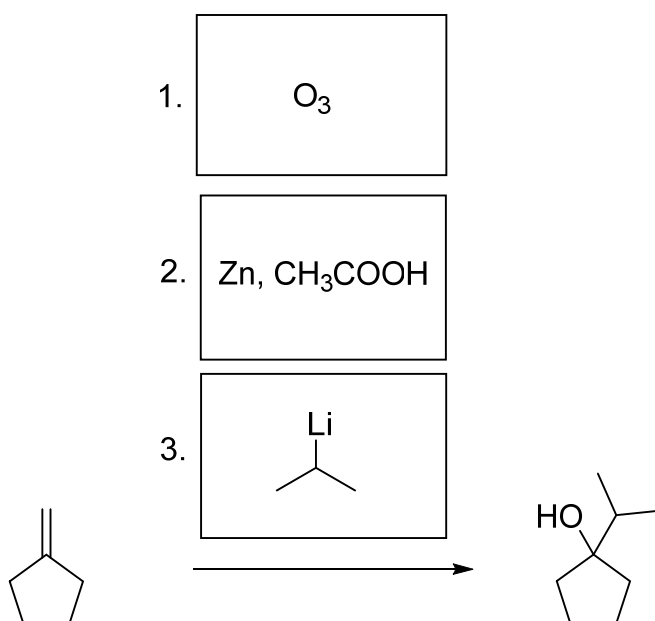
l.



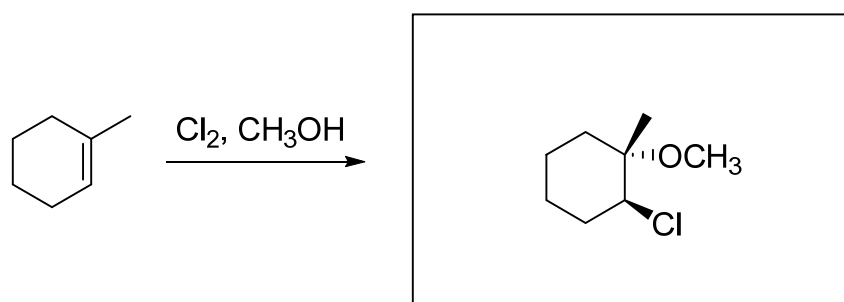
m.



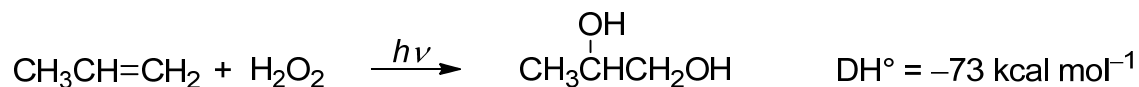
n.



o.

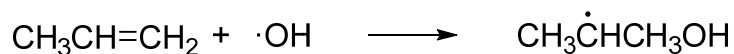


III. [50 Points] Another way to effect the vicinal dihydroxylation of alkenes is by a radical reaction with hydrogen peroxide. Consider the reaction of propene by this pathway.

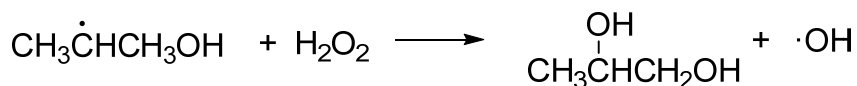


a. Write the two propagation steps for the radical chain reaction:

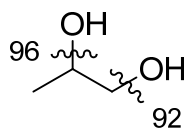
Step 1.



Step 2.



b. As indicated above, the ΔH° for this process equals $-73 \text{ kcal mol}^{-1}$. Considering the bond dissociation energies indicated below (DH° in kcal mol^{-1}) and the π bond strength (65 kcal mol^{-1}), estimate the O–O bond dissociation energy of H_2O_2 . Show your work.



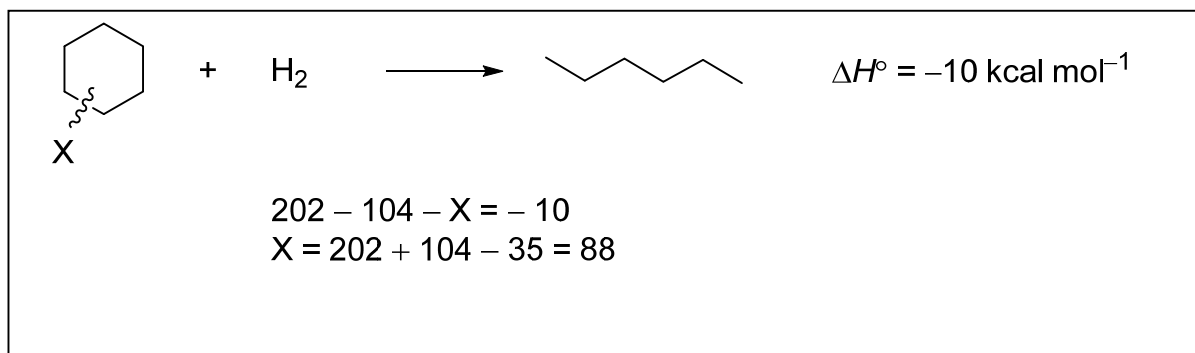
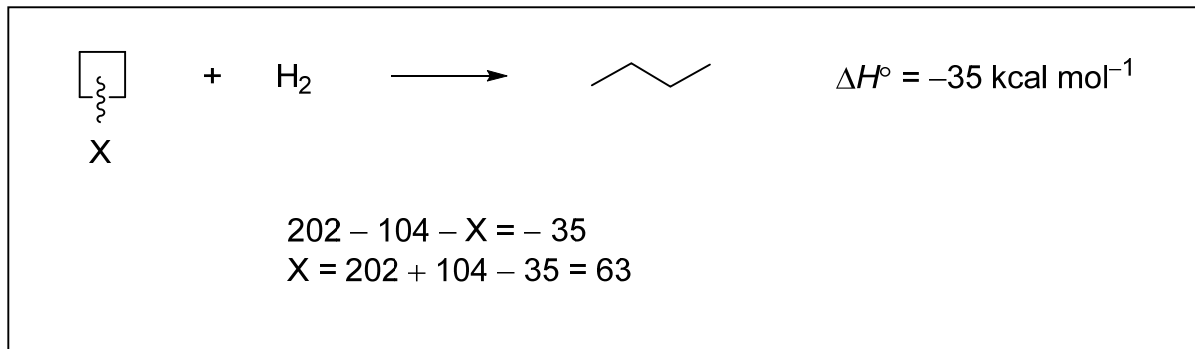
$$65 + X - 96 - 92 = -73$$

$$X = 96 + 92 - 65 - 73 = 50$$

c. The strength of the HO–OH bond is noticeably larger than that of CH₃O–OCH₃. Provide a possible explanation (one sentence).

The methyl group stabilizes the radical center by hyperconjugation

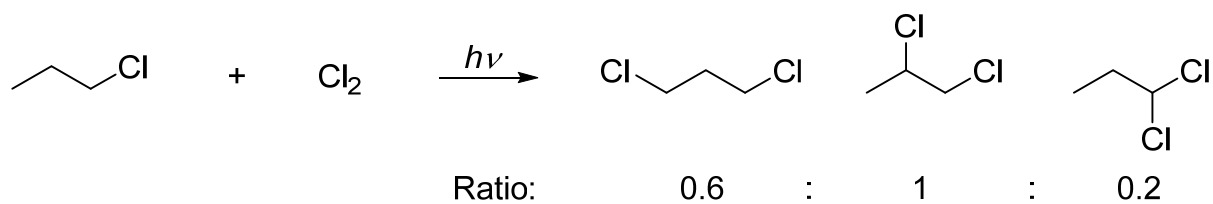
IV. [30 Points] Using the following data, estimate the C–C bond dissociation energy of cyclobutane and cyclohexane, respectively. Show your work.



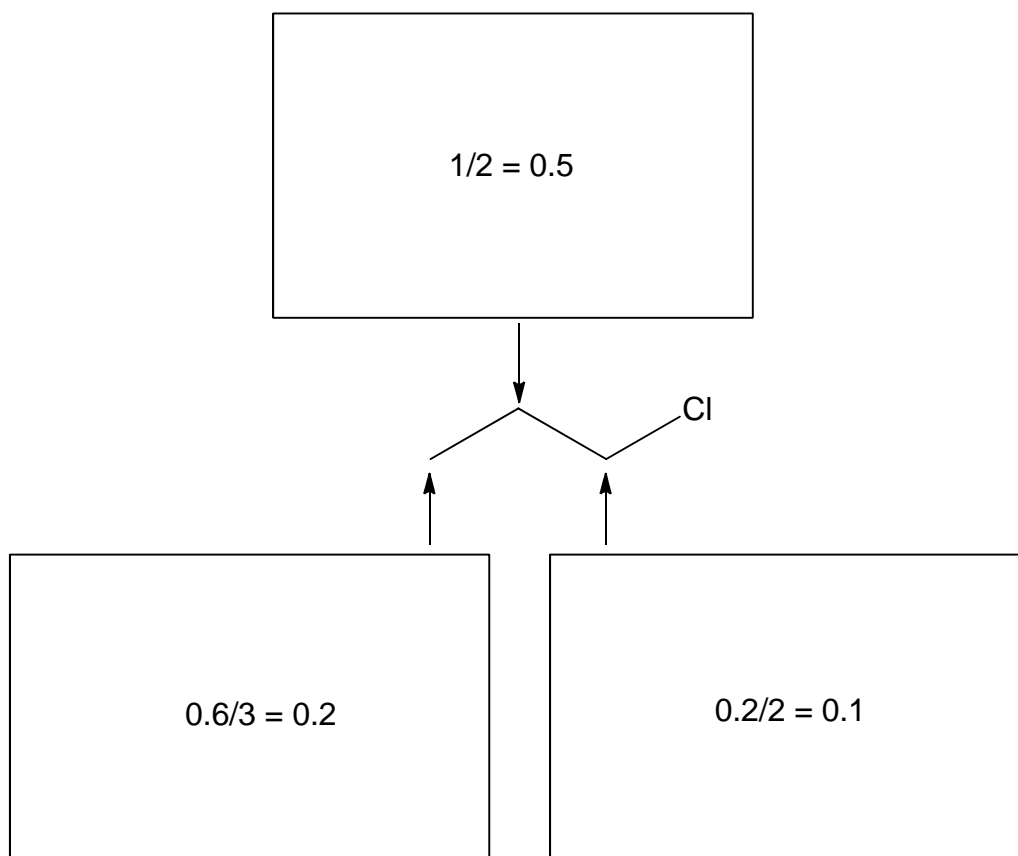
What is the ring strain (in kcal mol⁻¹) in cyclobutane?

25 kcal mol⁻¹

V. [30 Points] The radical chlorination of 1-chloropropane gives three products in the ratio shown below.

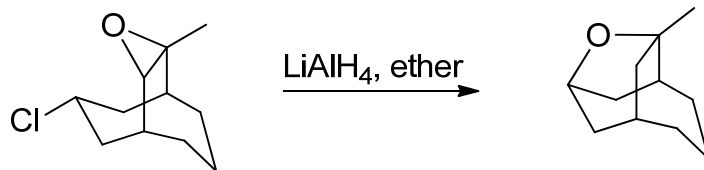


What is the relative selectivity of replacing a hydrogen with chlorine at the three carbons? In the individual boxes pertaining to the indicated position (arrow), show your work and your answer.

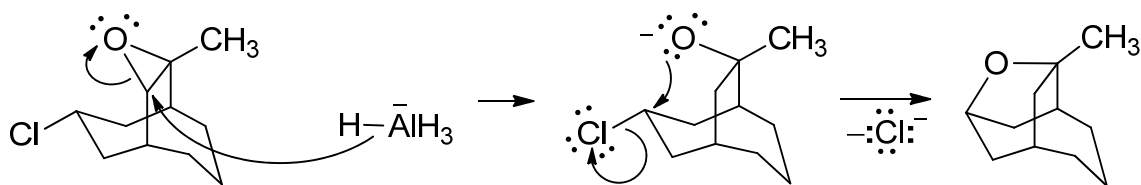


VI. [75 Points] Write detailed step-wise mechanisms for the following transformations. Use only structures and "arrow-pushing" techniques. Note: These are not synthetic problems. Do not add any reagents! What you see is what you have!

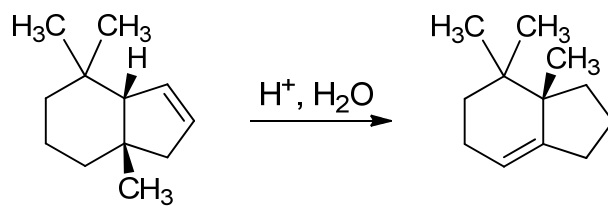
a.



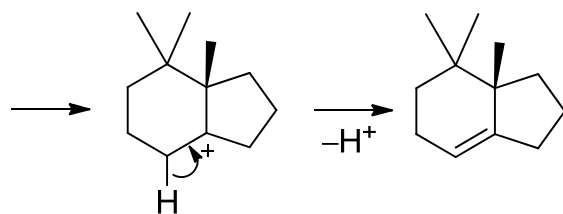
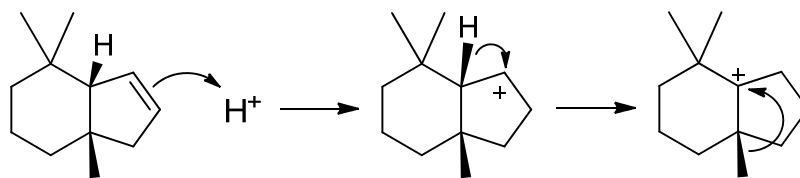
Work from left to right in the following spaces. There is much more space than you will need.



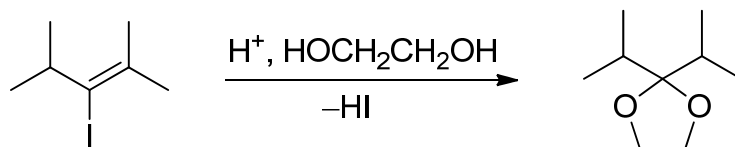
b.



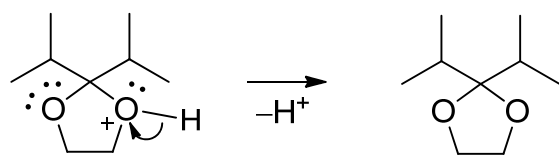
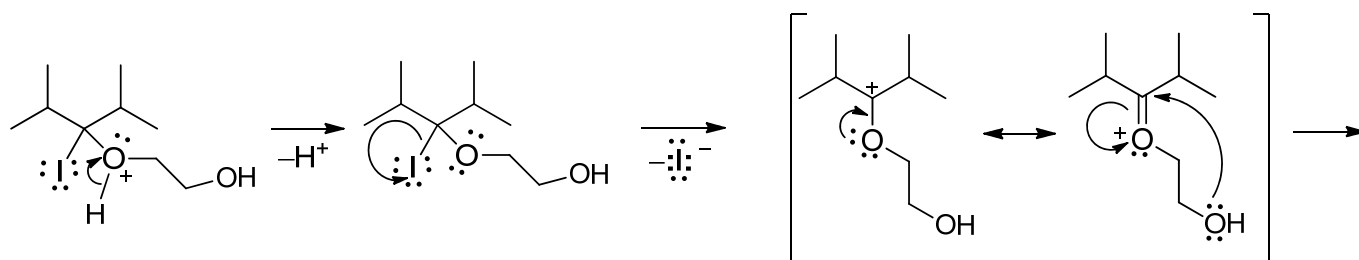
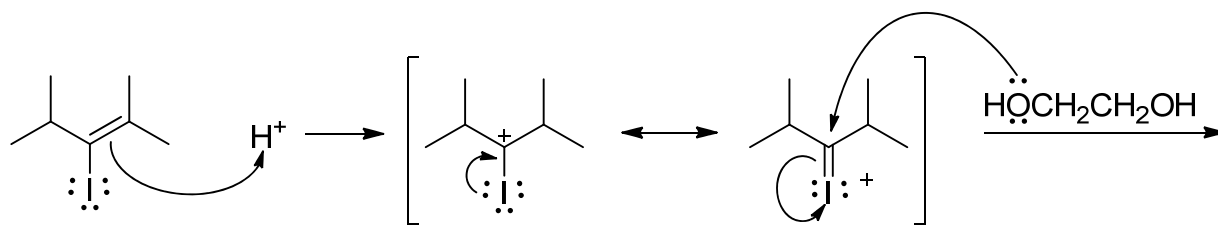
Work from left to right in the following spaces. There is much more space than you will need.



c.

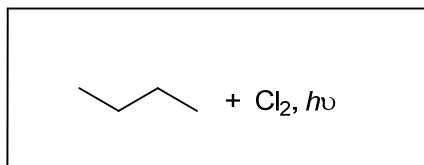
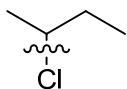


Work from left to right in the following spaces. There is much more space than you will need.



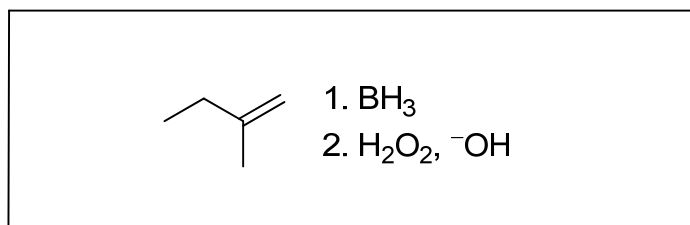
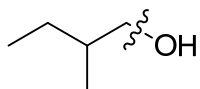
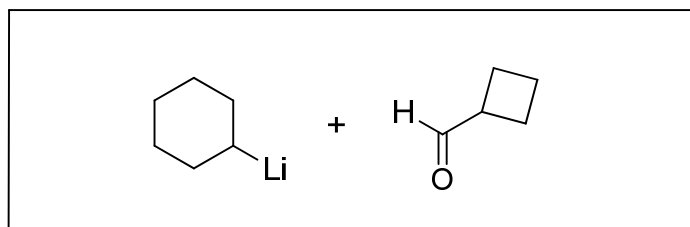
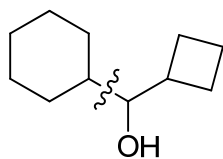
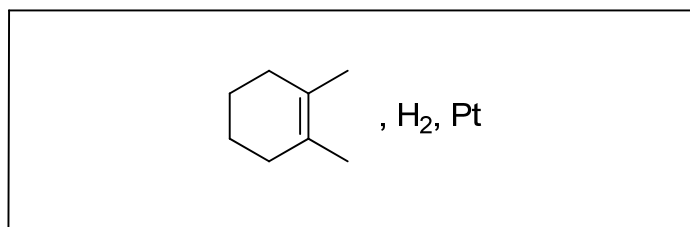
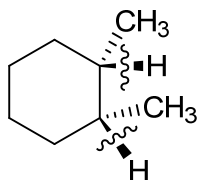
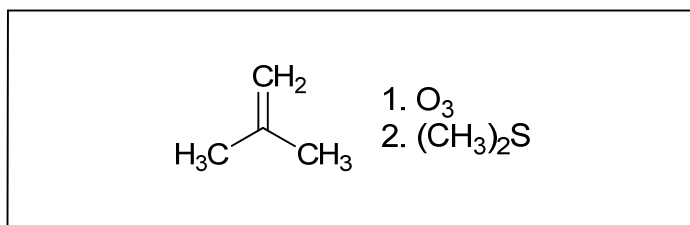
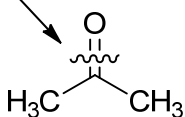
VII. [20 Points] For the following retrosynthetic disconnections (indicated by “~”), enter in the box provided the process that would make the ruptured bond. Follow the format indicated in the sample problem below.

Sample problem:



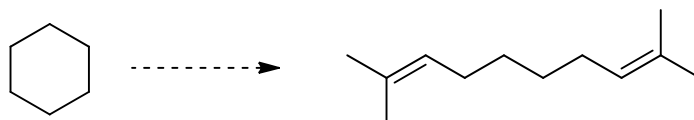
Problems to be answered:

Note: both bonds are cleaved

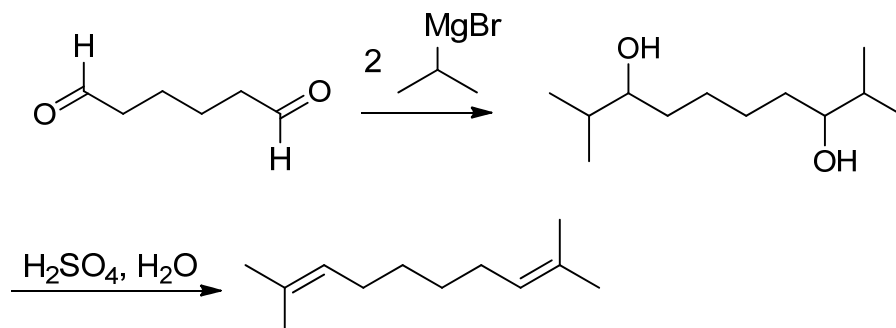
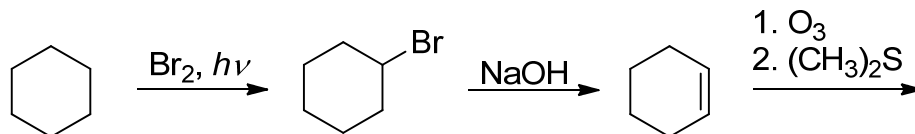


VIII. [75 Points] Show synthetic **forward connections** (reagents, intermediates; no mechanisms!) between the following starting materials and the final (racemic) products. Note: several steps are required in each case; there may be several solutions to each problem, but you should use only one; it is best to work backwards (retrosynthetically) on the back of the exam pages, to enable you to dissect the products into less complex precursors. However, the answer to be graded should be a *forward* scheme. In addition to the starting structure, you may use any organic and organometallic reagents **containing four carbons or less**.

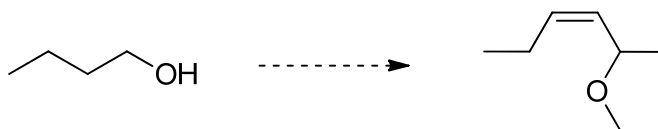
a.



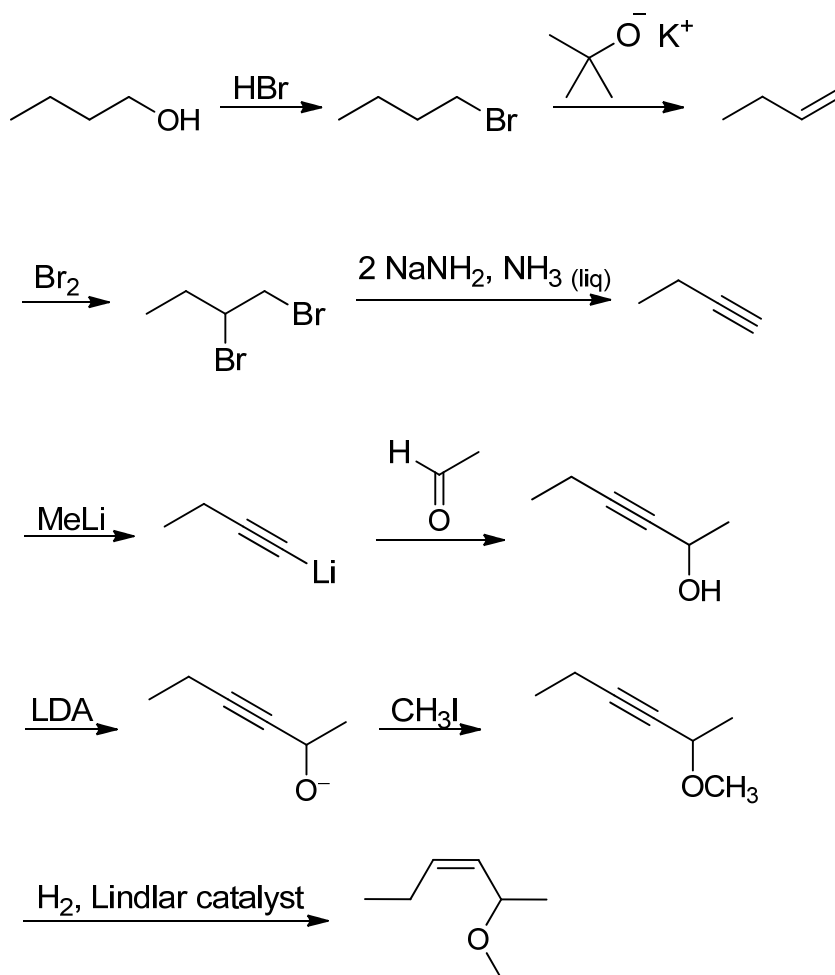
Work from left to right in the following spaces. There is much more space than you will need.



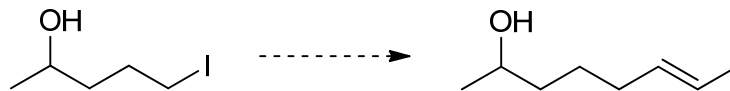
b.



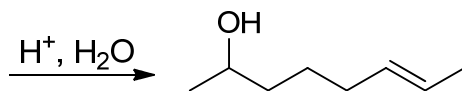
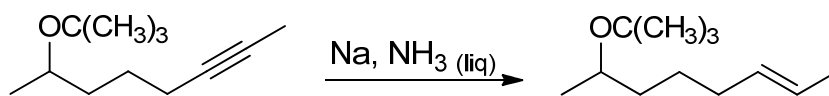
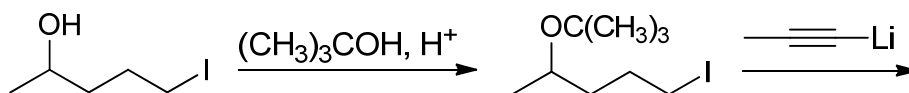
Work from left to right in the following spaces. There is much more space than you will need. Remember: In addition to the starting structure, you may use any organic and organometallic reagents **containing four carbons or less**.



c.

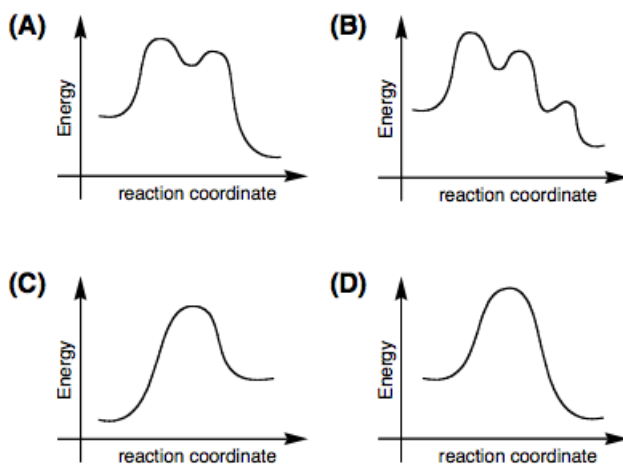


Work from left to right in the following spaces. There is much more space than you will need. Remember: In addition to the starting structure, you may use any organic and organometallic reagents **containing four carbons or less**.



IX. [37 Points]

a. Which of the following potential energy diagrams describes an E1 reaction? Give your answer (A, B, C, or D) in the box provided.



Answer:

A

b. The order of **increasing** acidity of 1–4 is:



Place an "X" mark next to your answer.

- 1, 2, 3, 4
 2, 4, 1, 3
 3, 1, 2, 4
 4, 2, 1, 3

c. *trans*-1,2-Dimethylcyclohexane is (place an "X" mark next to your answer in the box provided):

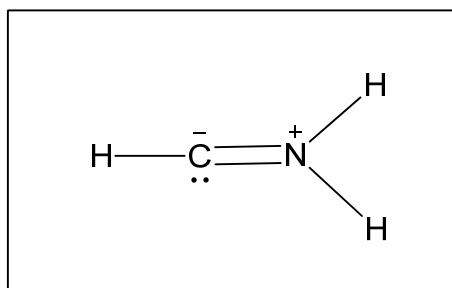
Achiral

Chiral

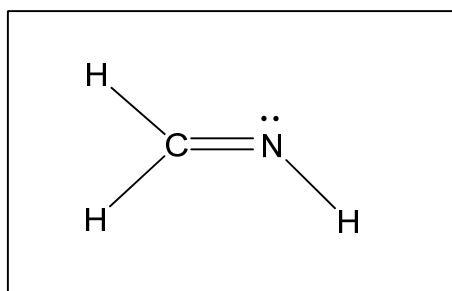
Chiral only at low temperatures

Achiral, because of rapid ring flip

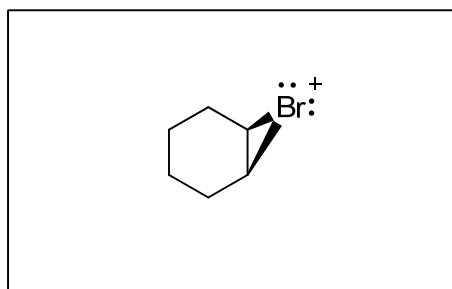
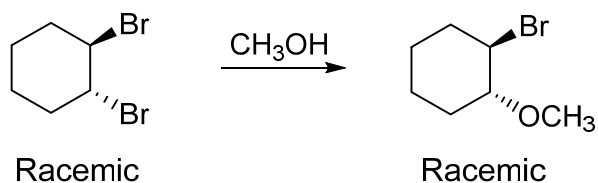
d. The carbene :CH_2 is a reactive six-electron species. Replacing one H with NH_2 gives a much more stable molecule. Explain by its most favorable resonance structure in the box below. You can use lines instead of electron pairs for bonds.

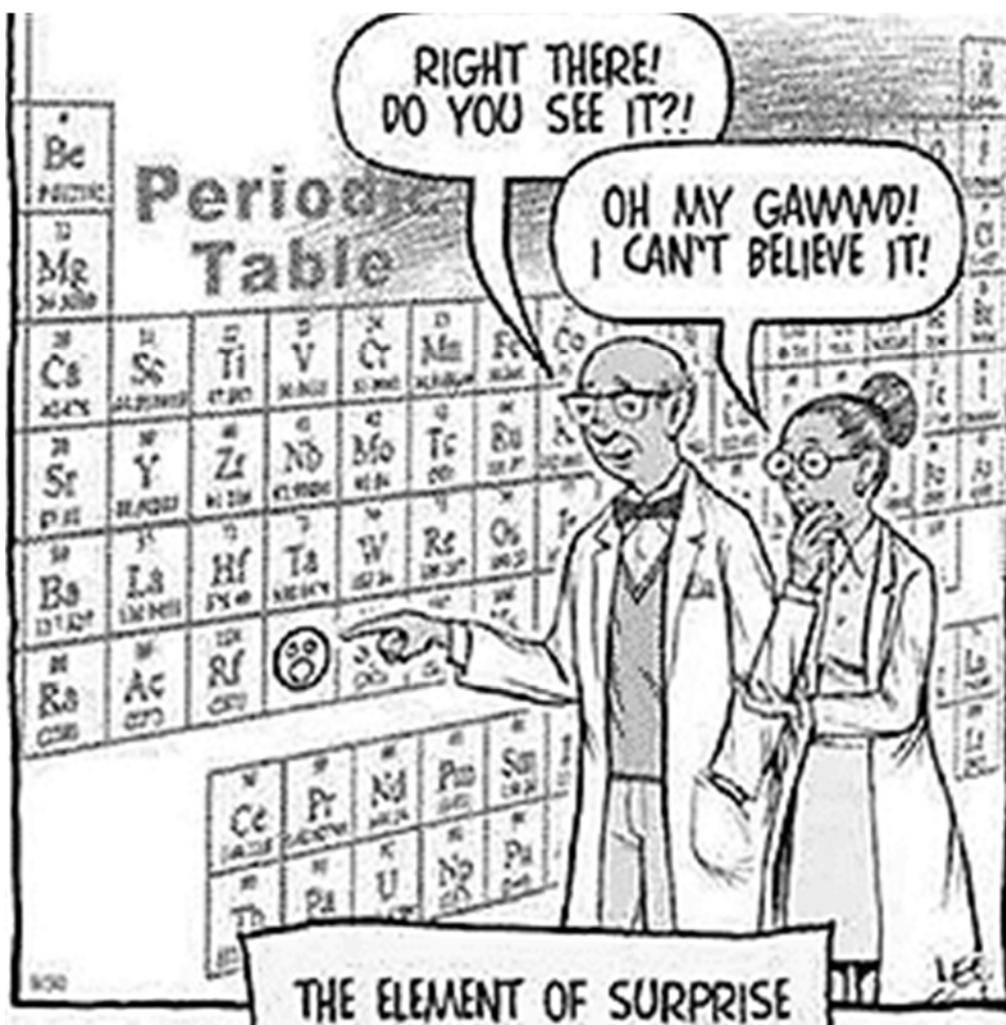


This molecule spontaneously undergoes tautomerization (proton shift) to an even more stable isomer. Draw its structure in the box below.



e. Methanol converts *trans*-1,2-dibromocyclohexane to *trans*-1-bromo-2-methoxycyclohexane stereospecifically. Draw the structure of the intermediate of this reaction that explains this selectivity in the box provided. Don't forget to show electron pairs around Br.





* The End *

Have a great summer!