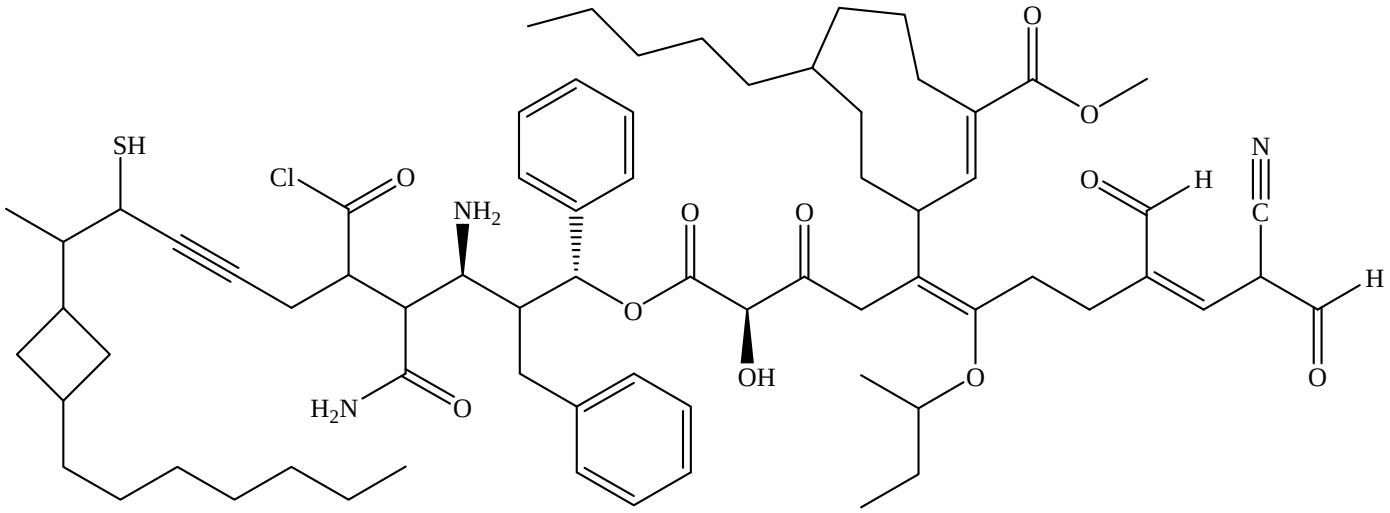
Chem 2010 Final
Fall, 2018 Name _____
Beauchamp

Problems	Points	Credit
1. Functional Group Nomenclature (1 large structure)	30	
2. 3D structure and resonance	20	
3. Combustion Reactions, Calculate $\Delta H_{combustion}$, using ΔH_f to compare kcal/gram	20	
4. Predict order of reactivity	20	
5. Reactions page (30)	30	
6. S_N/E 3D Mechanisms, with all of the details, Templates Provided	40	
7. Acid / Base Chemistry (1)	20	
8. Free Radical mechanism, ΔH, types of stereoisomers	20	
9. Cyclohexane Conformations, 2 substituents, Newman Proj, Rel. Energies OR Chain Conformations, Newman Proj, Rel. Energies	20	
10. Synthesis problem (1)	30	
11. Fill in all mechanistic details, curved arrows, lone pairs, formal charge,	20	
12. Carbocation Rearrangements	15	
Total	285	

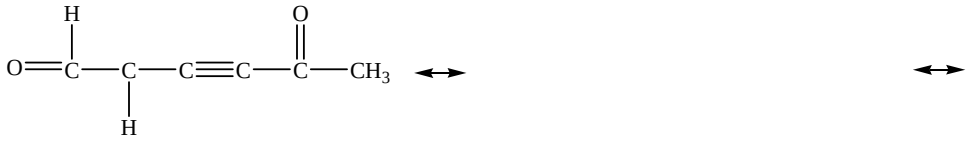
This is a long exam. It has been designed so that no one question will make or break you. The best strategy is to work steadily, starting with those problems you understand best. Make sure you show all of your work. Draw in any lone pairs of electrons, formal charge and curved arrows to show electron movement where appropriate. Do your best to show me what you know in the time available.

The opposite of a correct statement is a false statement. But the opposite of a profound truth may well be another profound truth. Niels Bohr

Provide an acceptable name for the following structure. Indicate the absolute configuration of any chiral centers shown in three dimensional form (R/S) and any E/Z stereogenic centers. (30 pts)



2. Draw two additional "**better**" 2D resonance structures of the given structure. Assume all nonhydrogen atoms have full octets unless + is written next to carbon. Add in any necessary lone pairs and use proper curved arrows to show electron movement. Which structure(s) is(are) best and why? Draw a 3D structure **for the given resonance structure**. Show bonds in front of the page as wedges, bonds in back of the page as dashed lines and bonds in the page as simple lines. Show orbitals for pi bonds and lone pairs along with their electrons. (20 pts)

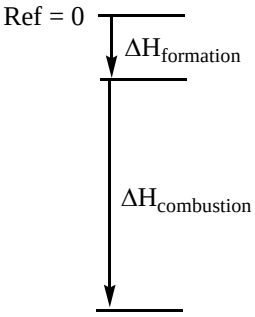


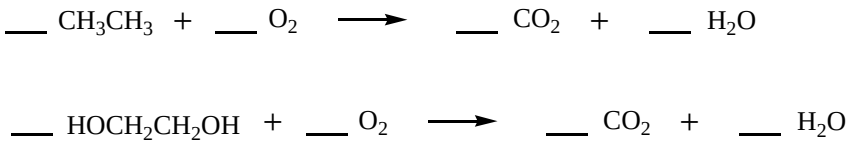
(6 pts)

(14 pts)

3. Given the following heats of formation (ΔH_f^o), calculate the energy of combustion in kcal per gram for ethane and ethylene glycol (ethan-1,2-diol). Which compound has more energy available per gram? Explain why they are so different. (20 pts)

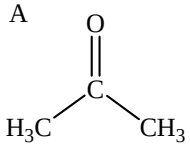
ΔH_f^o (ethane) = -20 kcal/mole
ΔH_f^o (ethylene glycol) = -110 kcal/mole
ΔH_f^o (CO_2) = -94 kcal/mole
ΔH_f^o (H_2O) = -57 kcal/mole
ΔH_f^o (O_2) = 0 kcal/mole
MW (CH_3CH_3) = 30 grams/mole
MW ($HOCH_2CH_2OH$) = 62 grams/mole



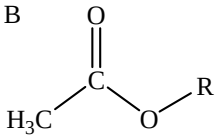


4. Predict the relative order of reactivity of the indicated carbonyl compounds in reactions with nucleophiles (1 = most reactive carbonyl electrophile). Use all three logic arguments of organic chemistry (resonance, inductive and steric). Show structures, lone pairs and arrow-pushing conventions in your answer to provide an explanation for your order of reactivity. Write the expected product in a reaction with lithium aluminium deuteride, $LiAlD_4$, followed by workup (no mechanisms). (20 pts)

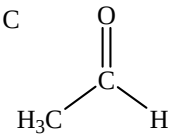
A



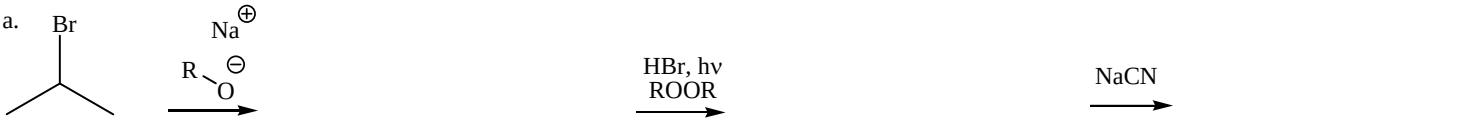
B

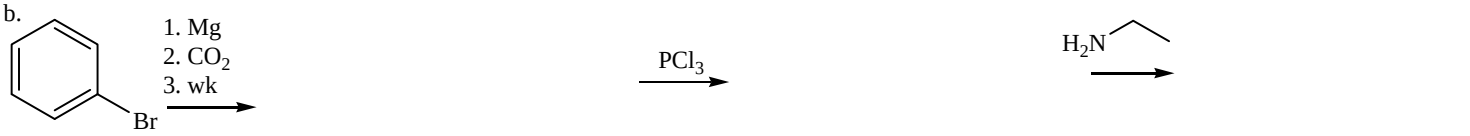


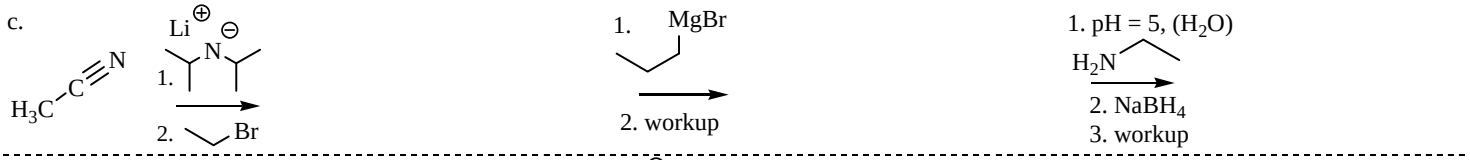
C

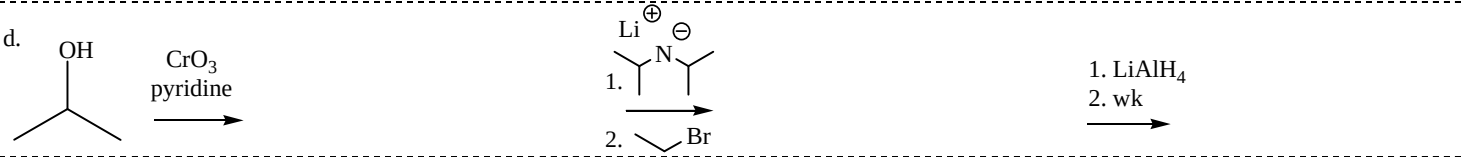


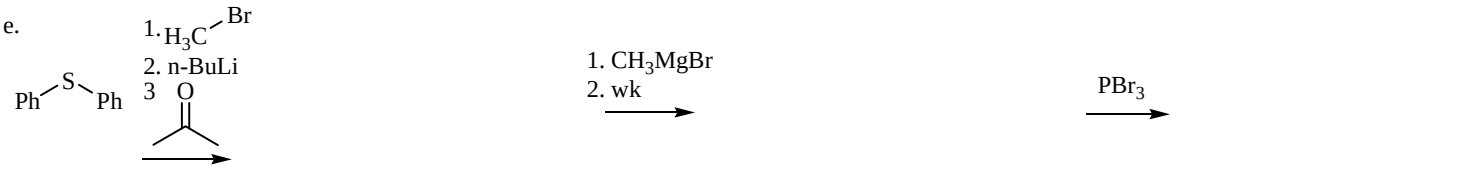
5. Fill in the missing product or reagent, as needed, for each reaction below. Do not waste time by writing mechanisms or thinking too much on any one part. (30 pts)

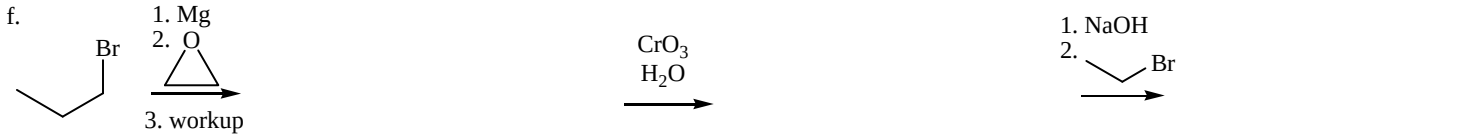
a. 

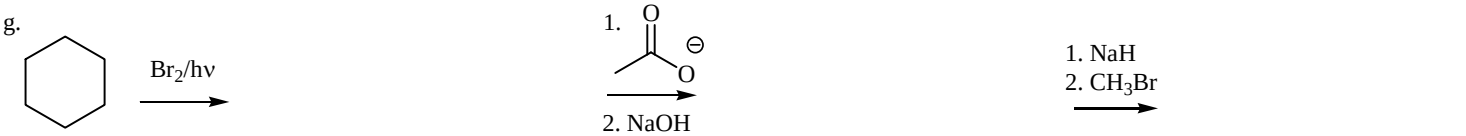
b. 

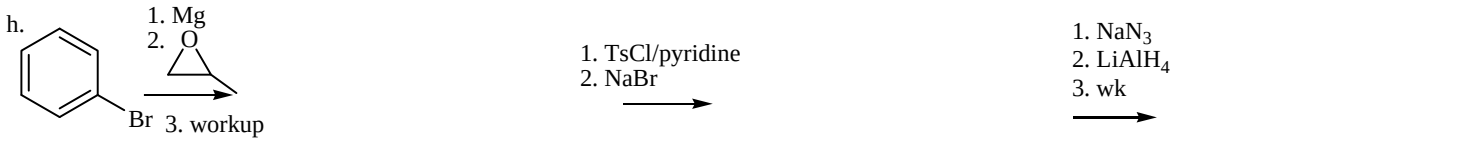
c. 

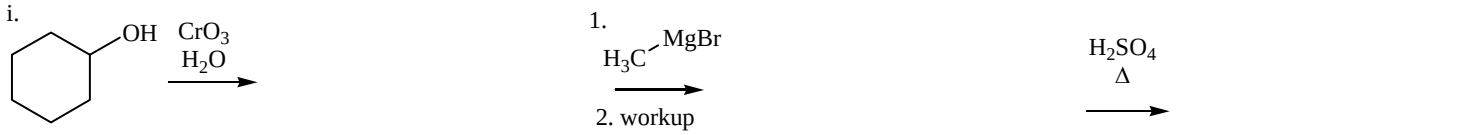
d. 

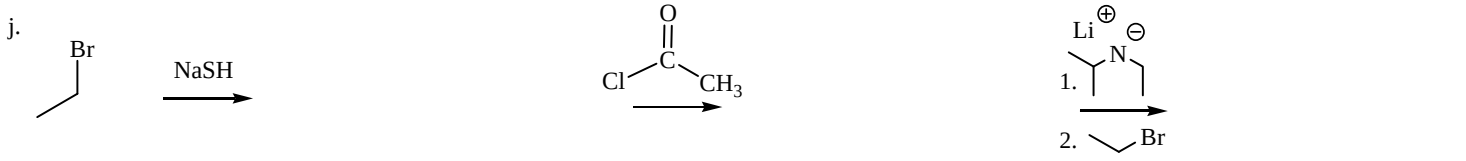
e. 

f. 

g. 

h. 

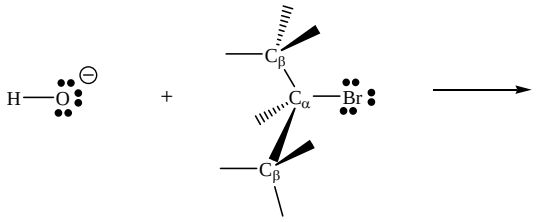
i. 

j. 

6. Use (2S,3R,4R)-2-deuterio-3-bromo-4-methylhexane to provide a simple, arrow-pushing mechanism for each of the following reaction conditions (show curved arrows, lone pairs & formal charge). Fill in the necessary details to clearly indicate any stereochemical features and/or conformational requirements. If reactants are not drawn in the proper orientation to show how the reaction must proceed, then redraw them in a more informative way that shows this. **Do not** consider carbocation rearrangement possibilities. (40 pts)

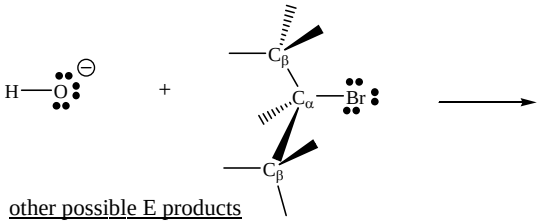
a. Draw a 2D structure and then a 3D structure of the reacting molecule. A 3D structure will be provided for the cost of the points of this part. (3 pts)

b. Show a mechanism for each C_β position and simply draw all other possible E reaction products (what kind?). Indicate if E, Z or neither. You can abbreviate common branch names if they are not part of your mechanism There may or may not be fewer products than there are numbers. (10 pts)



mechanism

E / Z configuration

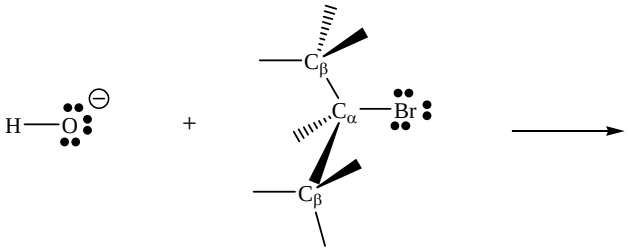


other possible E products

E / Z configuration

1 2 3 4 5

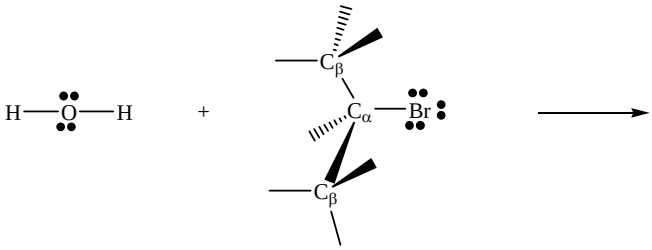
c. Show the S_N reaction (what kind?), indicate the absolute configuration(s) of the C_α center in the product. (6 pts)



mechanism

C_α configuration

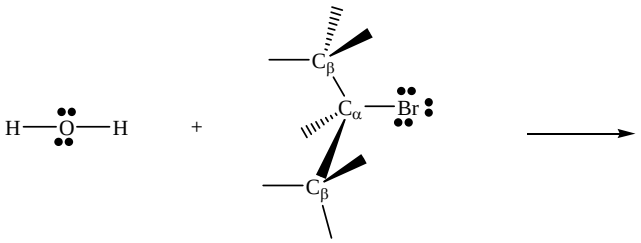
d. Show all steps of the S_N reaction (what kind?). You can use one intermediate to show all possible S_N possibilities. Indicate the absolute configuration(s) of the C_α center in the product. You can abbreviate common branch names if they are not part of your mechanism (9 pts)



mechanism

C_α configuration(s)

e. Show a mechanism for two E products and simply draw all other possible E reaction products (you can use the same intermediate for your two mechanisms). Indicate if E, Z or neither. There may or may not be fewer products than numbers. (12 pts)

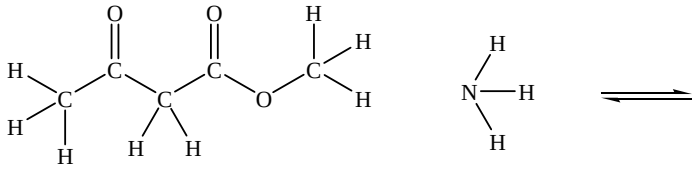


mechanism

E or Z

other possible E products

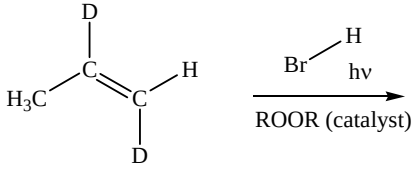
7. Show how the two compounds shown react in an acid / base reaction. Include all mechanism details (curved arrows, lone pairs and formal charge). The acid on the left side has a pK_a of 11 and the acid on the right side has a pK_a of 9. Decide which proton is most acidic on the left side, which also decides the reactant base. That will allow you to write the correct conjugate products. Explain why the proton you used is the most acidic proton. Calculate an equilibrium constant, K_{eq} for the reaction. (20 pts)



Two acid pK_a values = 9, 11

K_{eq} =

8. Write a mechanism to show the expected products for the reaction shown. Calculate a ΔH for each step of your mechanism and the overall reaction. How many stereoisomers are possible? What sorts of stereoisomer possibilities are there? You don't have to write out any 3D structures, but use R's and S's to indicated the types of stereoisomer possibilities. (20 pts)

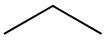
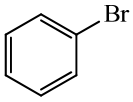


Important bond energies.	
RO-OR	ΔH = 40 kcal/mole
O–H	ΔH = 110 kcal/mole
H-Br	ΔH = 88 kcal/mole
CC pi	ΔH = 64 kcal/mole
C-H	ΔH = 95 kcal/mole
C-Br	ΔH = 68kcal/mole

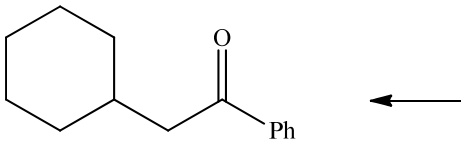
9. Draw all possible chair conformations of cis-1- phenyl-2-ethylcyclohexane. Make the left most ring carbon C_1 and number towards the front. Show **all** axial and equatorial groups in the first chair. Draw the more stable conformation first. Provide a reason for your answer. Draw a Newman projection of the least stable conformation using the $C_2 \rightarrow C_1$ and $C_4 \rightarrow C_5$ bonds to sight along. Point out any substituent gauche interactions shown in your Newman projection. The axial energy of an phenyl group is 2.8 kcal/mole and the axial energy of an ethyl group is 1.8 kcal/mole and a phenyl/ethyl gauche interaction is 1.5 kcal/mole, what is the ratio of the two conformations at equilibrium? Show your work. (20 pts)

b. Newman projection ($C_2 \rightarrow C_1$ and $C_4 \rightarrow C_5$) – least stable, point out any gauche interactions with the substituent(s)

10. Propose a reasonable synthesis for each of the following molecules. You must use the given starting materials and any reagents we have studied in our course. (30 pts)

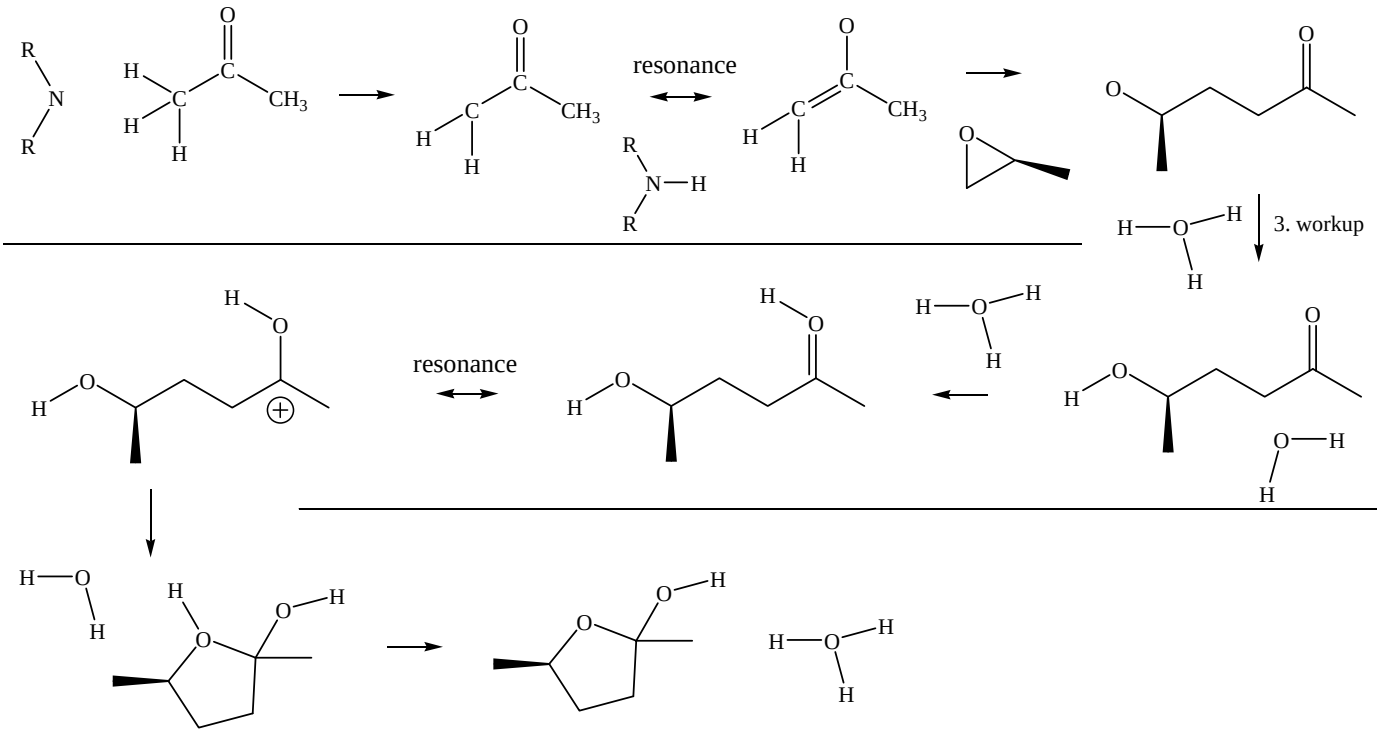
Given: CH_4    

NaCN CO_2

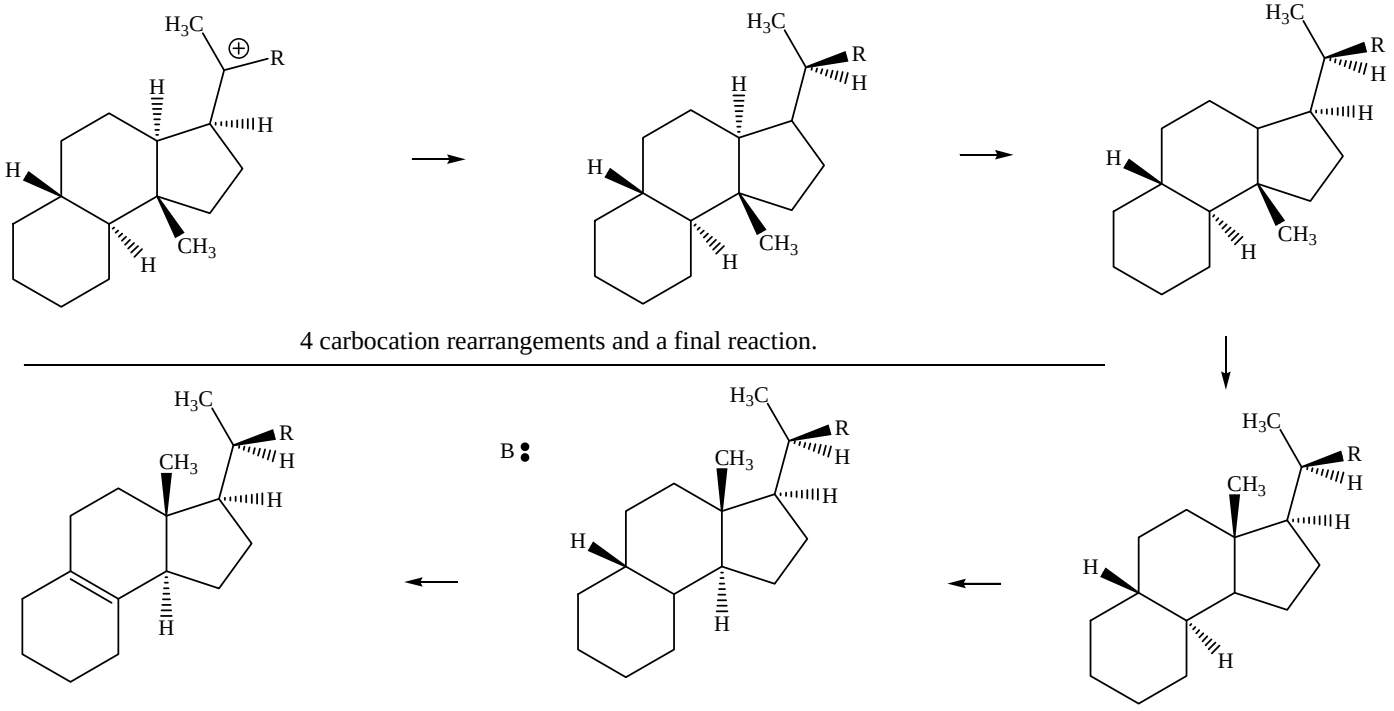


11. Provide all missing arrow-pushing mechanistic details (curved arrows, lone pairs and formal charge) to explain the following transformations. Assume all nonhydrogen atoms have full octets unless a positive charge is written by a carbon atom. (20 pts)

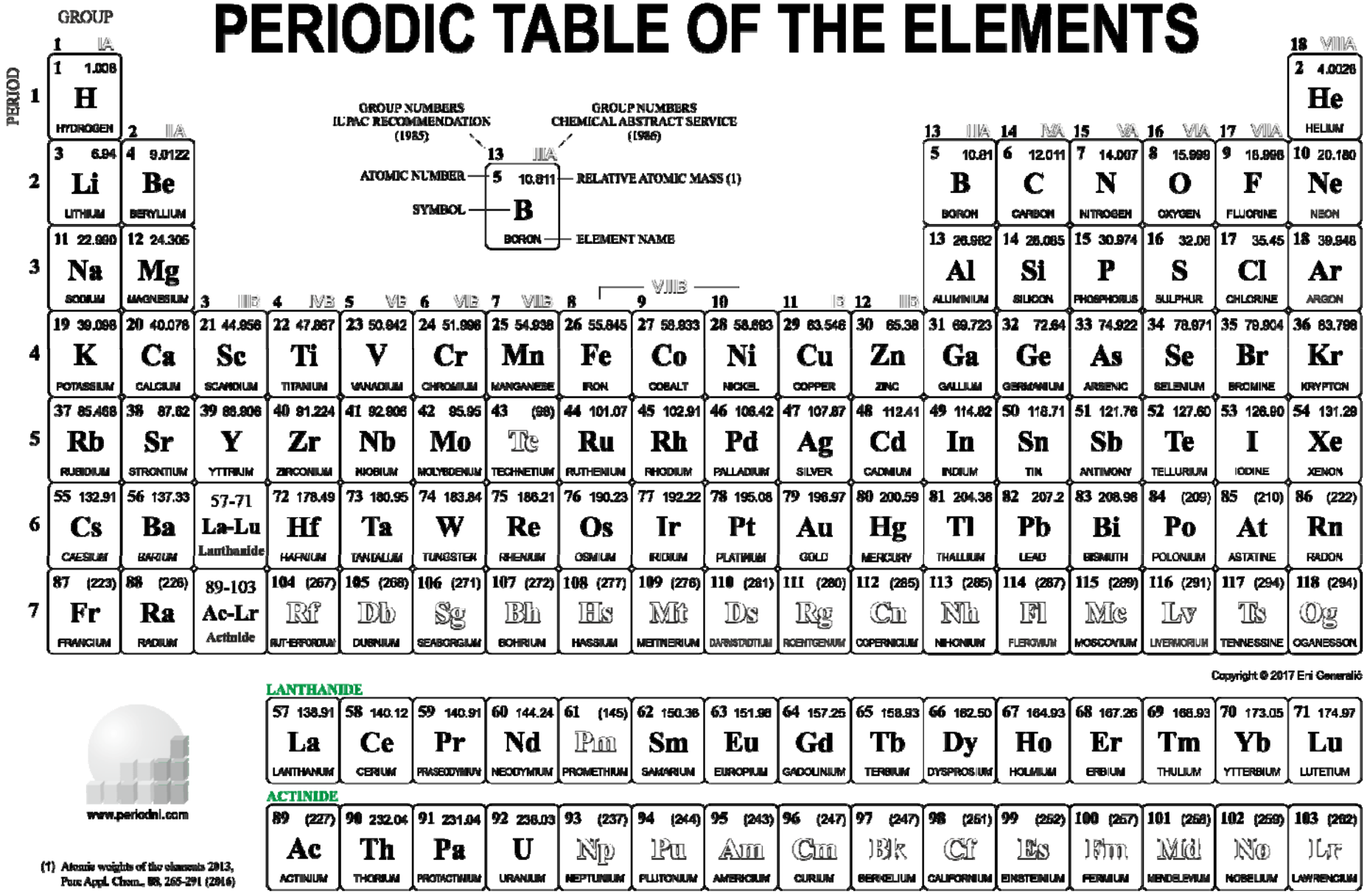
a.



12. Fill in the missing details to show how these 5 steps form lanosterol (only a partial structure is shown), which continues on to cholesterol in 19 additional steps. (15 pts)



The obstacle is the path. Zen Proverb


PERIODIC TABLE OF THE ELEMENTS
GROUP
PERIOD
GROUP NUMBERS IUPAC RECOMMENDATION (1985)
GROUP NUMBERS CHEMICAL ABSTRACT SERVICE (1986)
ATOMIC NUMBER
SYMBOL
RELATIVE ATOMIC MASS (1)
ELEMENT NAME
VIIIB
LANTHANIDE
ACTINIDE
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www.periodni.com
(1) Atomic weights of the elements 2013, Pure Appl. Chem., 88, 265-291 (2016)