

Chem 2010  
Midterm #2  
Fall, 2018  
Beauchamp

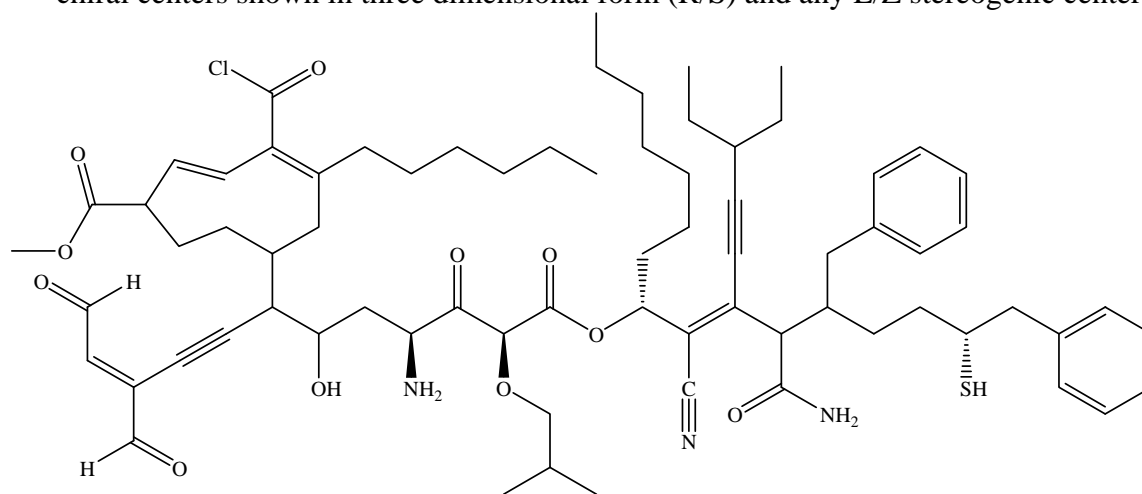
Name \_\_\_\_\_  
(Print your name legibly)

Problem	Points	Credit
1. Nomenclature (one structure)	30	
2. Explain relative stabilities based on logic arguments of organic chemistry	20	
3. Chair conformations or Chain conformations or Stereochemistry or 2D/3D structures, hybridization	25	
4 Acid/base equations, draw mechanism details, estimate $K_{eq}$ , explain answer	24	
5. $S_N$ and E mechanisms, including stereochemical details	40	
6. Predict products (20)	30	
7. Propose short syntheses (2)	30	
8. Carbocation rearrangement	15	
9. Free Radicals, Predict products provide mechanism	30	
<b>Total</b>	244	

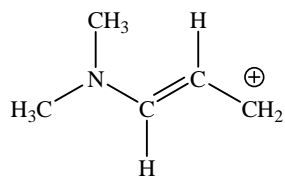
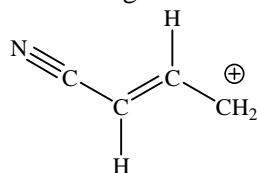
This is a long exam. It has been designed so that no one question will make or break you. The best strategy is to work steadily, starting with those problems you understand best. Make sure you show all of your work. Draw in any lone pairs of electrons, formal charge and curved arrows to show electron movement in mechanism and explanation problems. If resonance is part of an answer, draw the best resonance structure, plus at least one additional resonance structure to show that resonance is present. Only write answers in the space available. Do your best to show me what you know in the time available.

Your mission in life is not merely to survive, but to thrive; and to do so with some passion, some compassion, some humor and some style. Maya Angelou

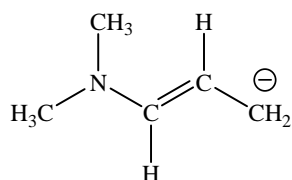
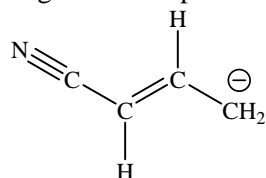
1. Provide an acceptable name for the following structure. Indicate the absolute configuration of any chiral centers shown in three dimensional form (R/S) and any E/Z stereogenic centers. (30 pts)



2. a. What is the most stable cation? Explain your reasoning, using structures, if necessary. Include curved arrows, formal charge and lone pairs. Hint: Consider the resonance of a  $C\equiv N$  group and a lone pair of electrons. (10 pts)



- b. What is the most stable anion? Explain your reasoning, using structures, if necessary. Include lone pairs, formal charge and lone pairs. Hint: Consider the resonance of a  $C\equiv N$  group and a lone pair of electrons. (10 pts)



3. a. Use Newman projections of the C3→C4 bond of 4-phenyl-2-methylhexane to show the lowest energy and highest energy conformations and calculate the relative energies. **Show the most stable conformation first.** Calculate a  $K_{\text{equilibrium}}$  between the least stable and most stable conformations. Assume  $R = 2 \text{ cal}/(\text{mol}\cdot\text{K})$  and  $T = 300 \text{ K}$ . (20 pts)

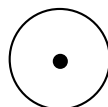
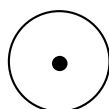
Approximate Eclipsing Energy Values (kcal/mole) Some were estimated by me.							
	H	Me	Et	i-Pr	t-Bu	Ph	Br
H	1.0	1.4	1.5	1.6	3.0	1.7	1.6
Me	1.4	2.5	2.7	3.0	8.5	3.3	2.8
Et	1.5	2.7	3.3	4.0	10.0	3.8	3.1
i-Pr	1.6	3.0	4.0	7.8	13.0	8.1	3.6
t-Bu	3.0	8.5	10.0	13.0	23.0	13.5	9.1
Ph	1.7	3.3	3.8	8.1	13.5	8.3	4.2
Br	1.6	2.8	3.1	3.6	9.1	4.2	3.0

Approximate Gauche Energy Values (kcal/mole) Some were estimated by me.							
	H	Me	Et	i-Pr	t-Bu	Ph	Br
H	0	0	0.1	0.2	0.5	0.2	0.1
Me	0	0.8	0.9	1.1	2.7	1.4	1.0
Et	0.1	0.9	1.1	1.6	3.0	1.7	1.2
i-Pr	0.2	1.1	1.6	2.4	3.5	2.1	1.6
t-Bu	0.5	2.7	3.0	3.5	7.2	3.9	3.3
Ph	0.2	1.4	1.7	2.1	3.9	2.7	1.9
Br	0.1	1.0	1.2	1.6	3.3	1.9	1.1

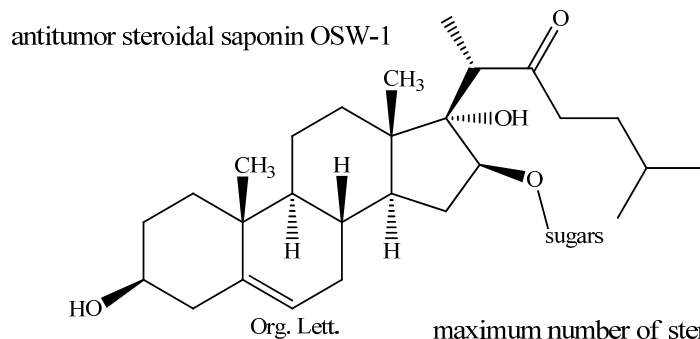
$$K_{\text{eq}} = 10^{\frac{-\Delta H}{2.3RT}}$$

most stable Newman  
Conformation

least stable Newman  
conformation

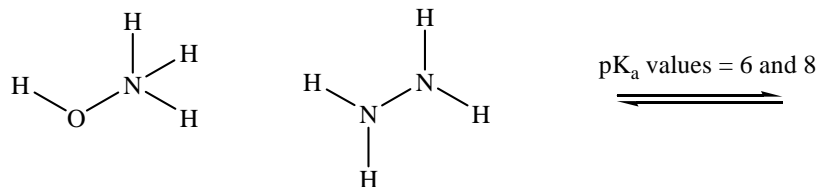


- b. Derivatives of the antitumor steroidal saponin were recently prepared. They are highly potent and selective anticancer compounds. They inhibit  $\text{Na}^+/\text{Ca}^{+2}$  exchange leading to higher  $\text{Ca}^{+2}$  in the cytosol and mitochondria causing cell death (apoptosis) (Org. Lett. ASAP, 2014). Circle all chiral centers and any other stereogenic features in the partial structure below, and calculate the maximum number of stereoisomers possible. (5 pts)

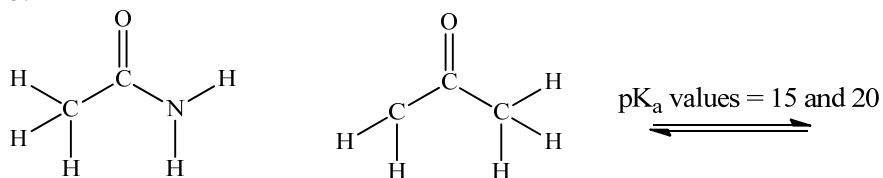


4. The reactant acids and bases are given in two acid/base equations below. Also given with each equation are two  $pK_a$  values. Complete each acid/base equation including any formal charge, lone pairs and curved arrows to show how the reactants react. Use the  $pK_a$  values to calculate a  $K_{eq}$  for each reaction. Provide a very brief explanation for which side is favored. Assume all nonhydrogen atoms have full octets. (24 pts)

a.

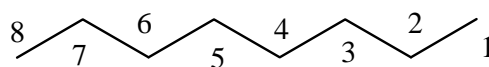


b.



5. Use 4*S*-bromo-5*R*-deuteriooctane 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)

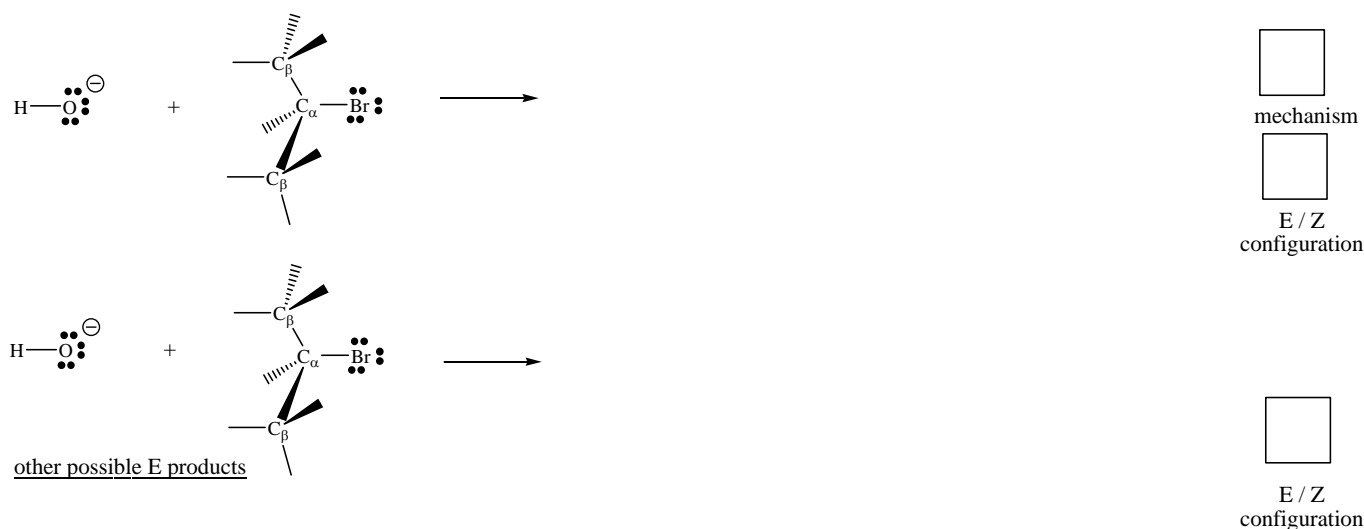
a. Draw a 2D structure and then a 3D structure of the reacting molecule. A 3D structure will be provided for the cost of the points of this part. (3 pts)



2D structure

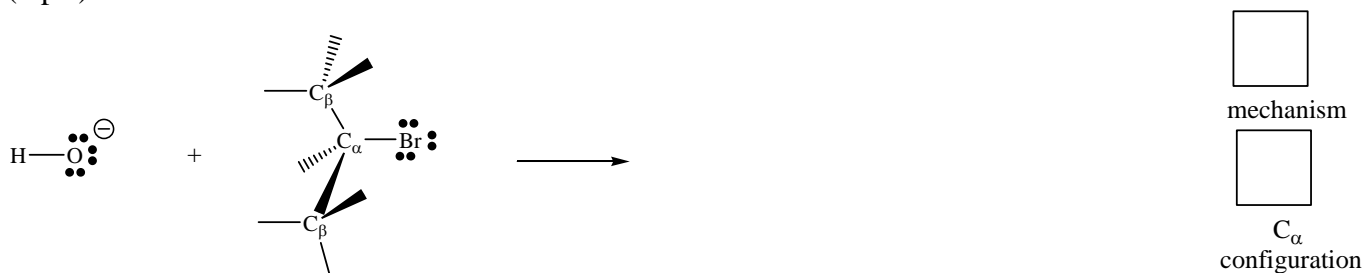
3D structure of (4*S*,5*R*)-5-deuterio-4-bromooctane

b. Show a mechanism for each  $C_{\beta}$  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)

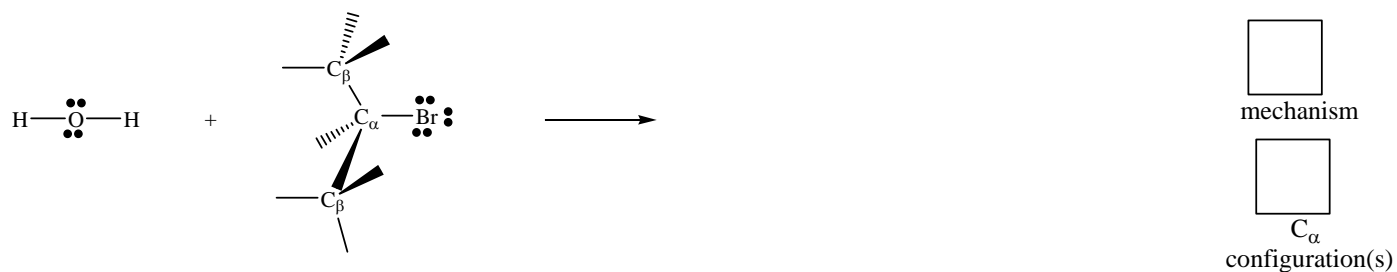


1 2 3 4 5

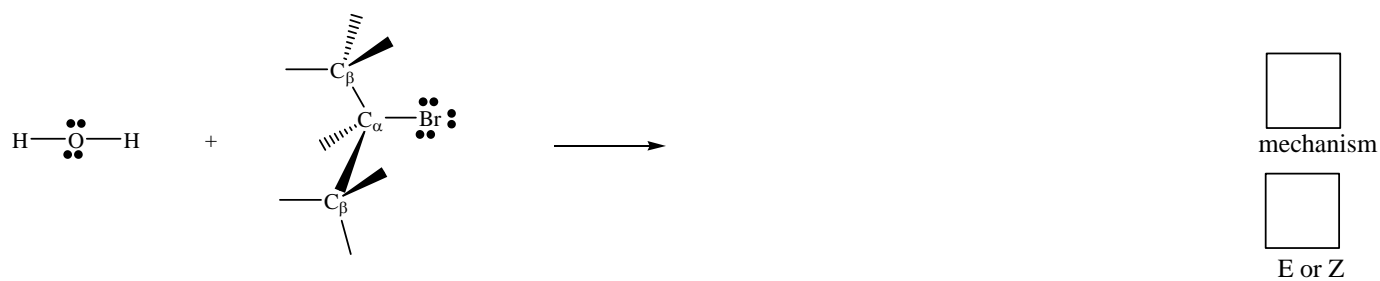
c. Show the  $S_N$  reaction (what kind?), indicate the absolute configuration(s) of the  $C_{\alpha}$  center in the product. (6 pts)



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  $C_\alpha$  center in the product. You can abbreviate common branch names if they are not part of your mechanism (9 pts)



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)



other possible E products

1

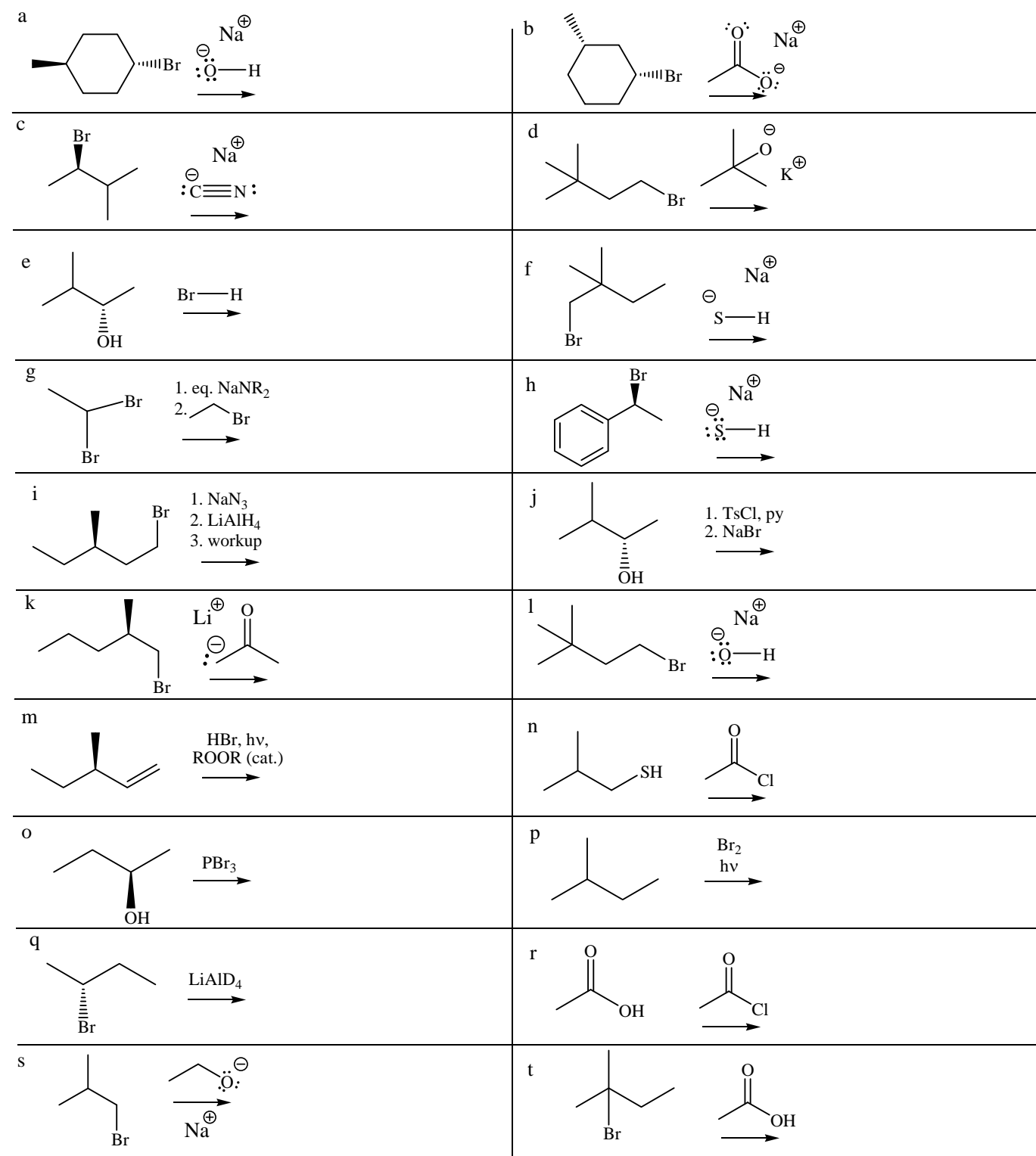
2

3

4

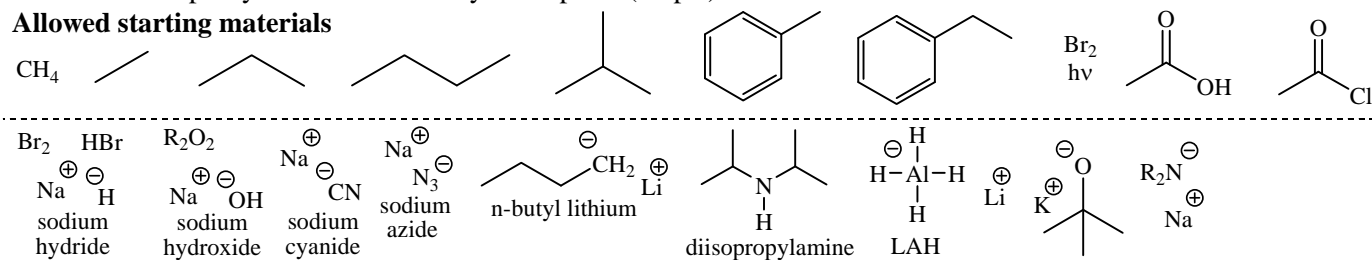
5

6. Write in the major product and type of reaction for each set of conditions below. Arrow pushing is not required (1.5 each, 30 pts)

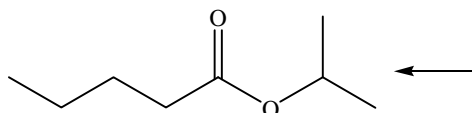


7. Propose a reasonable synthetic sequence to make the given target molecules using the given starting materials. Show each step with an arrow and the necessary reagents to accomplish the indicated transformation. If you make a molecule in one part you can use it in another part. (30 pts)

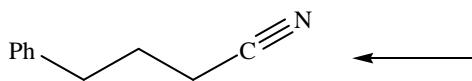
**Allowed starting materials**



a.

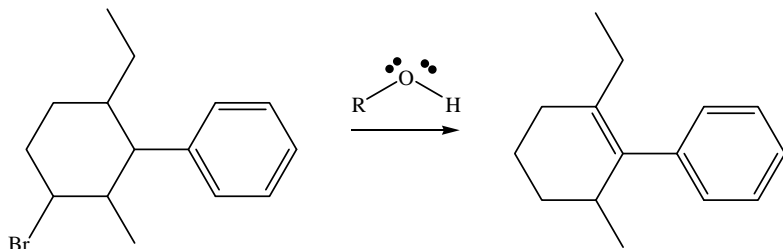


b.



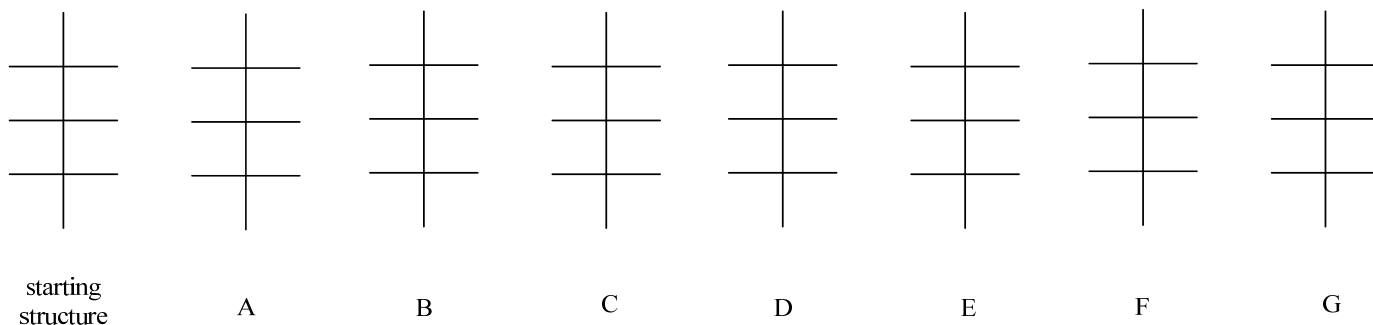
8. Propose a complete arrow-pushing mechanism for the following transformation. (15 pts)

c.





9. a. How many different types of  $sp^3$  hydrogen atoms are present in 2S-bromopentane? Show all possible products when 2S-bromopentane is brominated with  $Br_2/h\nu$ ? Use Fischer projections. Put a dot by any chiral centers. If stereoisomers form, specify what type of isomerism is present (enantiomers, diastereomers, meso compounds, achiral, etc.). Indicate the approximate relative amounts of each product formed if the relative rates of reaction of a bromine atom with an  $sp^3$  C-H bond are: primary = 1, secondary = 80, tertiary = 1600 and bromine substituted carbon = 2000. (21 pts)



enantiomers =  
 diastereomers =  
 meso =

- b. Provide a complete arrow pushing mechanism to explain formation of the major product from the above reaction (show proper curved arrow conventions, lone pairs as two dots and single electrons as one dot). Clearly label each distinct part of the reaction mechanism. Calculate an overall  $\Delta H$  for each step of your mechanism using the given bond energies. (15 pts)

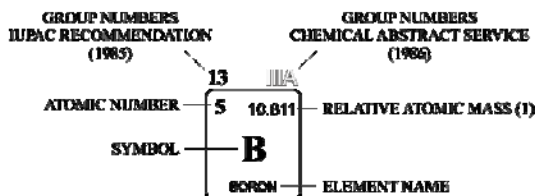
Br—Br	46
H—Br	88
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CH <sub>3</sub> -H	105
1° C-H	98
2° C-H	95
3° C-H	92
C <sub>α</sub> Br-H	88
-----	
CH <sub>3</sub> -Br	70
1° C-Br	68
2° C-Br	67
3° C-Br	66
C <sub>α</sub> Br-Br	64

It is in your moments of decision that your destiny is shaped.

Tony Robbins

# PERIODIC TABLE OF THE ELEMENTS

PERIOD	1	GROUP																18		
	1	1 IA																	2 VIIIA	
	1	1 1.008																	2 4.0026	
	2	3 6.94	4 9.0122																	10 20.180
	2	Li	Be																	Ne
		LITHIUM	BERYLLIUM																	NEON
	3	11 22.990	12 24.305																	18 39.948
3	Na	Mg																	Ar	
	SODIUM	MAGNESIUM																	ARGON	
4	19 39.098	20 40.078	21 44.956	22 47.867	23 50.942	24 51.998	25 54.938	26 55.845	27 58.933	28 58.933	29 63.546	30 65.38	31 69.723	32 72.64	33 74.922	34 78.971	35 79.904	36 83.798		
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr		
	POTASSIUM	CALCIUM	SCANDIUM	TITANIUM	VANADIUM	CHROMIUM	MANGANESE	IRON	COBALT	NICKEL	COPPER	ZINC	GALLIUM	GERMANIUM	ARSENIC	SELENIUM	BROMINE	KRYPTON		
5	37 85.468	38 87.62	39 88.906	40 91.224	41 92.906	42 95.95	43 (98)	44 101.07	45 102.91	46 106.42	47 107.87	48 112.41	49 114.82	50 118.71	51 121.76	52 127.60	53 126.90	54 191.22		
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe		
	RUBIDIUM	STRONTIUM	YTTORIUM	ZIRCONIUM	NIOBIUM	MOLYBDENUM	TECHNETIUM	RUTHENIUM	RHODIUM	PALLADIUM	SILVER	CADMIUM	INDIUM	TIN	ANTIMONY	TELLURIUM	IODINE	XENON		
6	55 132.91	56 137.33	57-71	72 178.48	73 180.95	74 183.84	75 186.21	76 190.23	77 192.22	78 196.08	79 198.07	80 200.59	81 204.38	82 207.2	83 208.98	84 (209)	85 (210)	86 (222)		
6	Cs	Ba	La-Lu Lanthanide	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn		
	CAESIUM	BARIUM		HAFNIUM	TANTALUM	TUNGSTEN	RHENIUM	OSMIUM	IRIDIUM	PLATINUM	GOLD	MERCURY	THALLIUM	LEAD	BISMUTH	POLONIUM	ASTATINE	RADON		
7	87 (223)	88 (226)	89-103	104 (267)	105 (268)	106 (271)	107 (272)	108 (277)	109 (276)	110 (281)	111 (280)	112 (285)	113 (285)	114 (287)	115 (289)	116 (291)	117 (294)	118 (294)		
7	Fr	Ra	Ac-Lr Actinide	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og		
	FRANCIUM	RADIUM		RUFORDIUM	DUBNIUM	SEABORGIUM	BOHRIUM	HASSIUM	MEITNERIUM	DARWINIUM	ROSGENIUM	COPERNICIUM	NIBOLIUM	FLEROVIUM	MOSCOWIUM	LIVERMORIUM	TENNESSEIUM	OGANESSONIUM		



LANTHANIDE

57 138.91	58 140.12	59 140.91	60 144.24	61 (145)	62 150.36	63 151.96	64 157.25	65 158.93	66 162.50	67 164.93	68 167.26	69 168.93	70 173.05	71 174.97
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
LANTHANUM	CERIUM	PRASEODYMIUM	NEODYMIUM	PROMETHIUM	SAMARIUM	EUROPIUM	GADOLINIUM	TERBIUM	DYSPROSIUM	HOLMIUM	ERBIUM	THULIUM	YTTERIUM	LUTETIUM

ACTINIDE

89 (227)	90 232.04	91 231.04	92 238.03	93 (237)	94 (244)	95 (243)	96 (247)	97 (247)	98 (251)	99 (252)	100 (257)	101 (258)	102 (259)	103 (262)
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
ACTINIUM	THORIUM	PROCTINIUM	URANIUM	NEPTUNIUM	PLUTONIUM	AMERICIUM	CURIUM	BERKELIUM	CALIFORNIUM	ENSTENIUM	FERMIUM	MENDELEVIUM	NOBELIUM	LAWRENCIUM



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(1) Atomic weights of the elements 2013, Pure Appl. Chem., 88, 265-291 (2016)