Chem 314
Final Exam
Spring, 2013
Beauchamp

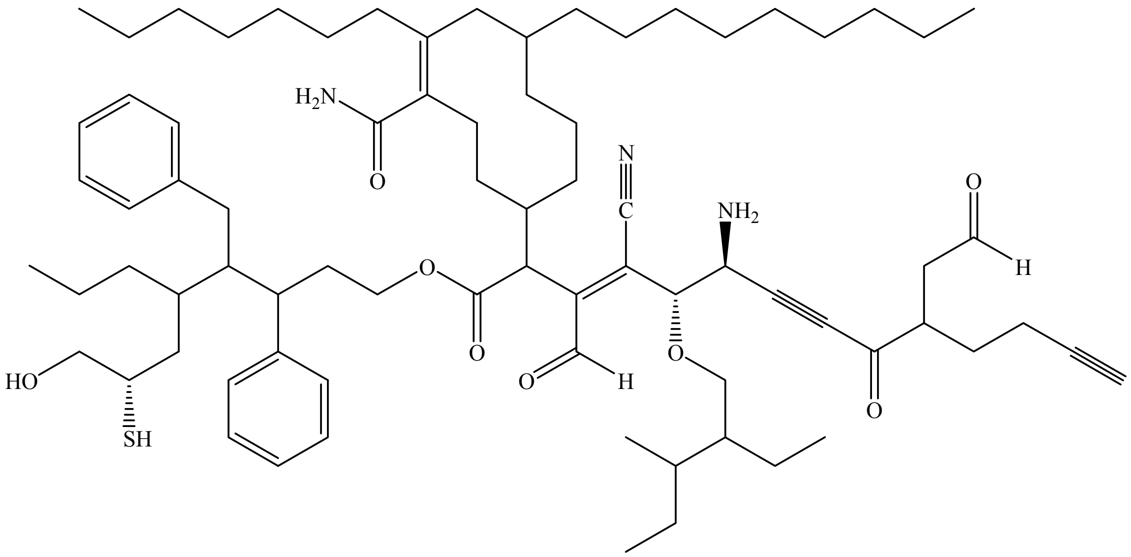
Name ___________________________________

Problem	Points	Credit
1. Nomenclature (one structure)	30	
2. 2D Lewis structure (large structure with possible formal charge)	20	
3. 3D Structures, Formal Charge, Resonance, Curved Arrows, Hybridization	34	
4. Cyclohexanes, Conformations, Configurations, Stereoisomers, Newman Projection	32	
5. Open chain conformations, Newman projections energy calculations	12	
6. Bond energy calculations and explanation	15	
7. Stereochemisty Questions	40	
8. Acid/Base Chemistry (arrow pushing, explanation)	34	
9. Explanation	16	
10. S_N and E mechanisms, including stereochemical details	40	
11. Synthesis of four synthetic target molecules (7 choices)	24	
12. Free Radicals, Predict products provide mechanism	36	
Total	333	

This is a long exam. It has been designed so that no one question will make or break you. You are not expected to completely finish the exam. 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. Do you best to show me what you know in the time available.

Human life is purely a matter of deciding what's important to you. ~ Anonymous

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)



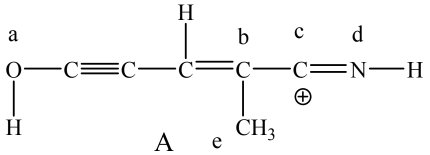
2. Draw an acceptable 2D Lewis structure for the following formula. Indicate any formal charges present. (20 pts)

6 carbon ring present

formal charge in this group

$OHCCCCHCCH_3O_2CCHNH_2COC_6H_4C(CH_3)_2CONHCH(COCH_3)CHCNCHNO_2CH(CONH_2)CH(CHO)CH(OCH_3)CH(COCl)CO_2H$

3. First, draw four other 2D resonance structures to delocalize any formal charge present. Include proper curved arrow conventions, including lone pairs and formal charge. Rank your structures from best (= 1) to poorest. Draw a three-dimensional Lewis structure of "A" and the best other resonance structure. Show sigma bonds as lines, wedges and dashes and the 2p orbitals in pi bonds as well as any orbitals holding lone pairs. Draw 2 dots for lone pair and π bond electrons. Use structure A to fill in the table at the bottom. **Assume that all nonhydrogens atoms have full octets, unless a carbocation is written**. (34 pts)



A ↔ B ↔ C

↕

E ↔ D

3D (A) 3D (best other)

Use structure A to fill in the following table.

	hybridization	angles	shape	#σ bonds	#π bonds	# lone pairs
a						
b						
c						
d						
e						

4. a. Draw both chair conformations of trans-2-methyl-1-t-butylcyclohexane and cis-2-methyl-1-t-butylcyclohexane. Make carbon #1 the left-most atom in your ring, and number towards the front. Indicate the approximate ΔH for each conformation (use the axial energy table on this page and the gauche energy table on the next page). Show all axial and equatorial groups at substituted ring carbons. What are the absolute configurations of all stereogenic atoms in chair 1? (20 pts)

⇌
cis

⇌
trans

chair 1
(absolute
congifigurations?)

chair 2

chair 3

chair 4

most stable (1 or 2) = _______

most stable (3 or 4) = _______

most stable overall (1,2,3,4) = _______

least stable overall (1,2,3,4) = _______

Axial Energy Values (kcal/mole)	
-Br	+0.5
$-CH_3$	+1.7
$C(CH_3)_3$	+5.0
gauche	use table

sterochemical relationship of 1 with 2? enantiomer, diastereomer, meso, identical, none

sterochemical relationship of 1 with 3? enantiomer, diastereomer, meso, identical, none

sterochemical relationship of 1 with 4? enantiomer, diastereomer, meso, identical, none

sterochemical relationship of 3 with 4? enantiomer, diastereomer, meso, identical, none

b. Use the most stable conformation from part a and draw a Newman projection using bonds $C_2 \rightarrow C_1$ and $C_4 \rightarrow C_5$ for your structure (indicate which chair you are using from part a, (chair 1,2,3,4). Point out any gauche relationships in the branches. (4 pts)

Newman projection of the most stable conformation from part a

c. Using dibromohexane, draw all of the chair conformations of two stereoisomers that have stereogenic centers, but do not have any chiral centers. Indicate the highest energy and the lowest energy chair conformations. What is the energy difference between them (use the above table and show your work). (8 pts)

⇌

⇌

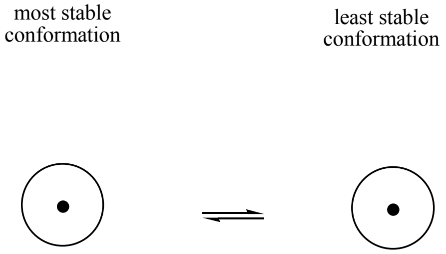
chair 1

chair 2

chair 3

chair 4

5. Use Newman projections of the C4→C3 bond of 2,3,5-trimethylhexane to show the lowest energy and highest energy conformations and calculate the relative energies. **Show the most stable conformation first**. Calculate a $K_{equilibrium}$ between the least stable and most stable conformations. Assume R = 2 cal/(mol-K) and T = 300 K. (12 pts)



Approximate Eclipsing Energy
Values (kcal/mole)

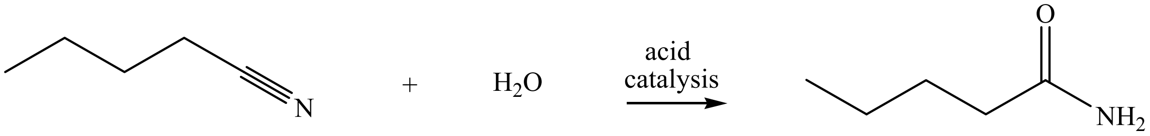
	H	Me	Et	i-Pr	t-Bu	Ph
H	1.0	1.3	1.4	1.6	3.0	1.7
Me	1.3	2.5	2.7	3.0	8.5	3.3
Et	1.4	2.7	3.3	4.5	10.0	3.8
i-Pr	1.6	3.0	4.5	7.8	13.0	8.1
t-Bu	3.0	8.5	10.0	13.0	23.0	13.5
Ph	1.7	3.3	3.8	8.1	13.5	8.3

Approximate Gauche Energy
Values (kcal/mole)

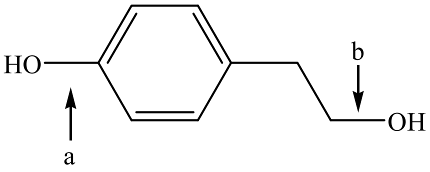
	H	Me	Et	i-Pr	t-Bu	Ph
H	0	0	0.1	0.2	0.5	0.2
Me	0	0.8	0.9	1.1	2.7	1.4
Et	0.1	0.9	1.1	1.6	3.0	1.5
i-Pr	0.2	1.1	1.6	2.0	4.1	2.1
t-Bu	0.5	2.7	3.0	4.1	8.2	3.9
Ph	0.2	1.4	1.5	2.1	3.9	2.3

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

6. a. Calculate the heat of reaction for the equation below using the **average** bond energies on the last page. Hint: You may need to solve for a pi bond energy. (9 pts)



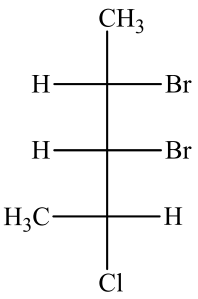
d. Find approximate bond energy values for the 2 carbon-oxygen bonds pointed out in the following structure using the bond energies in the **typical** substitution patterns table at the end of this exam. Suggest a rationale for any observed differences. Draw additional structures, if appropriate to your explanation. (6 pts)



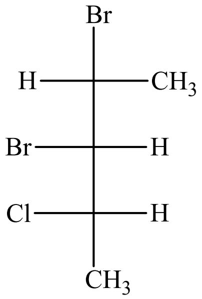
a =

b =

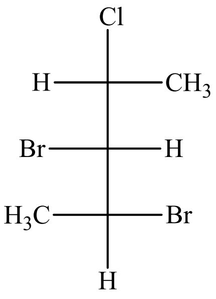
7. For the following set of Fischer projections answer each of the questions below by circling the appropriate letter(s) or letter combination(s). Hint: Redraw the Fischer projections having the longest carbon chain in the vertical direction and having similar atoms in the top and bottom portion. Classify all chiral centers in the first structure as R or S absolute configuration. (15 pts)



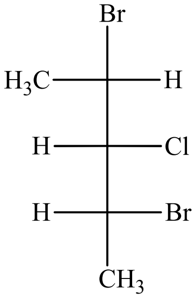
A



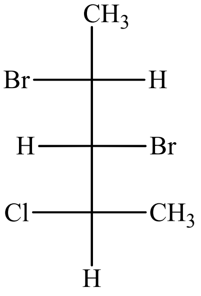
B



C



D



E

a. Which are meso? A B C D E

b. Which is not an isomer with the others? A B C D E

c. Which pairs are enantiomers? AB AC AD AE BC BD BE CD CE DE

d. Which pairs are identical? AB AC AD AE BC BD BE CD CE DE

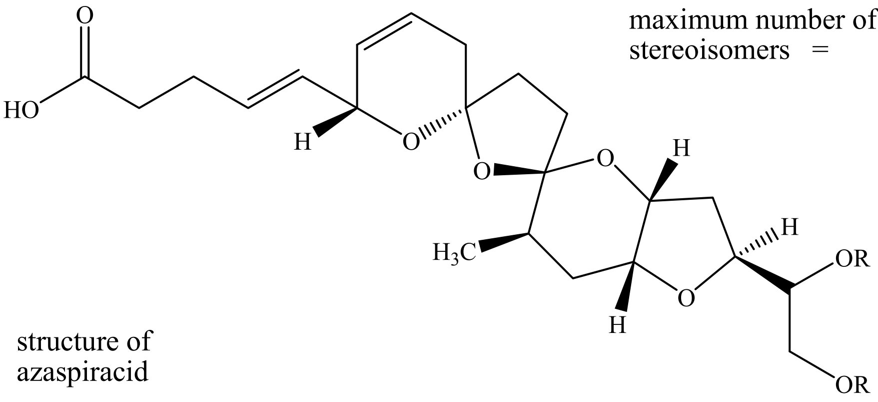
e. Which pairs are diastereomers? AB AC AD AE BC BD BE CD CE DE

f. Which would not rotate plane polarized light when mixed as a 50/50 racemic mixture?

AB AC AD AE BC BD BE CD CE DE

g. Draw Fischer projections of any stereoisomers of "A" which are not shown above. If there are none, indicate this. (6 pts)

h. The $C_1 - C_{21}$ segment of azaspiracid was recently synthesized. It is a marine toxin that has stimulated intense synthetic activity for pharmacological studies (Org. Lett. p.2338, 2013). Circle all chiral centers and any other stereogenic features in the partial structure below, and calculate the maximum number of stereoisomers possible. (4 pts)

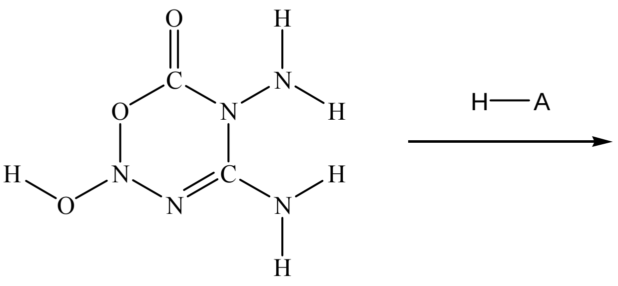


maximum number of stereoisomers = _______________

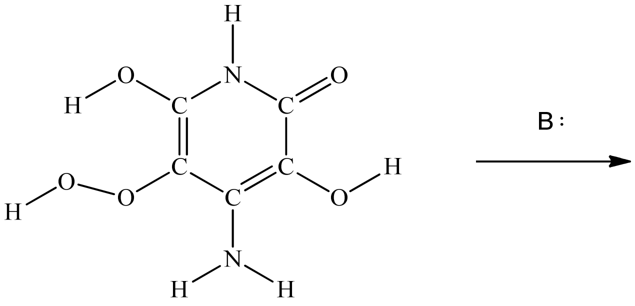
structure of azaspiracid

8. Each molecule below can act as either an acid or a base (they are amphiprotic). Use a general acid, HA, and show molecule 1 acting as a base at its most basic site. Use a general base, B:, and show molecule 2 reacting as an acid at its most acidic site. Use curved arrows to show the flow of electrons and include formal charge and lone pairs. Draw all resonance structures important to the conjugate acid or base. Provide a brief explanation for why your "acid" and "base" is the "best" choice. (12 pts each)

a. reaction in acid, HA

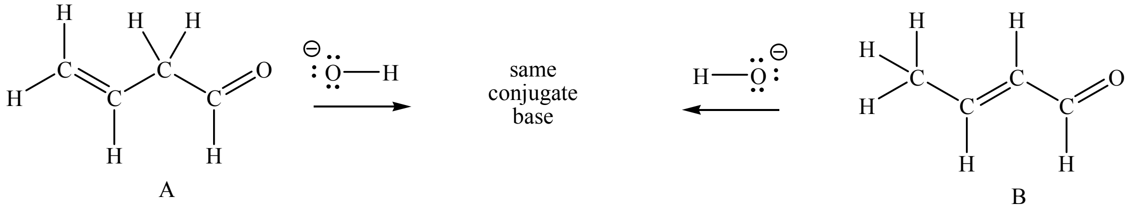


b. reaction in base, B:

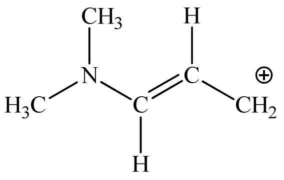


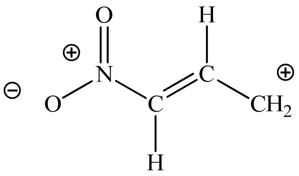
2

d. Acids A and B have different structures, but share a common conjugate base. Draw curved arrows to show how the proton transfer occurs in each case and explain why the conjugate base is the same for each acid. (10 pts)

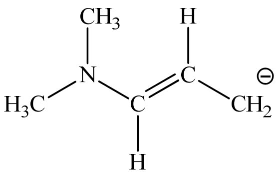


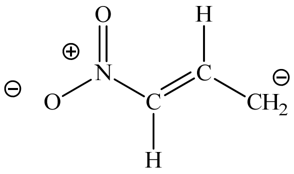
9. a. What is the most stable cation? Explain your reasoning, using structures, if necessary. (8 pts)





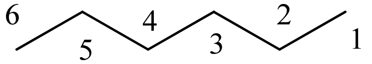
b. What is the most stable anion? Explain your reasoning, using structures, if necessary. (8 pts)





10. Use 2R-deuterio-3R-bromo-4S-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, since we did not cover them. (40 pts)

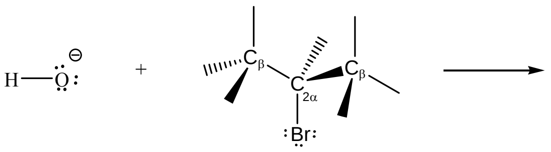
a. Draw a 2D structure and then a 3D structure of the reacting molecule. A 3D structure will be provided for the cost of the points of this part. (3 pts)



2D structure

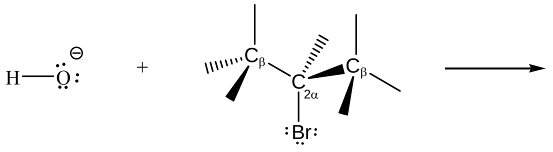
3D structure of (2R,3R,4S)-2-deuterio-3-bromo-4-methylhexane

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 (12 pts)



☐ mechanism

☐ E / Z configuration



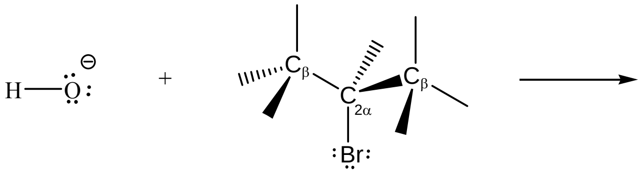
other possible E products

☐ E / Z configuration

1 2 3 4 5

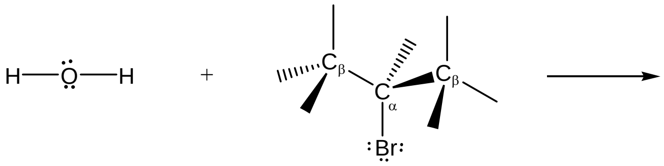
c. Show the S_N reaction (what kind?), indicate the absolute configuration(s) of the C_α center in the product. (6 pts)

☐ mechanism



☐ C_α configuration

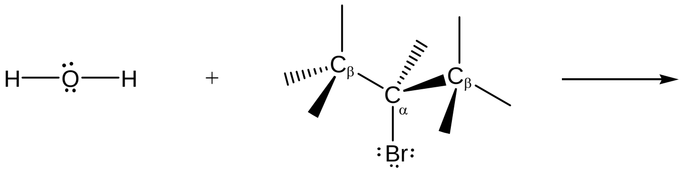
d. Show all steps of the S_N reaction (what kind?). You can use one intermediate to show all possible S_N possibilities. Indicate the absolute configuration(s) of the C_α center in the product. You can abbreviate common branch names if they are not part of your mechanism (9 pts)



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. (10 pts)



mechanism

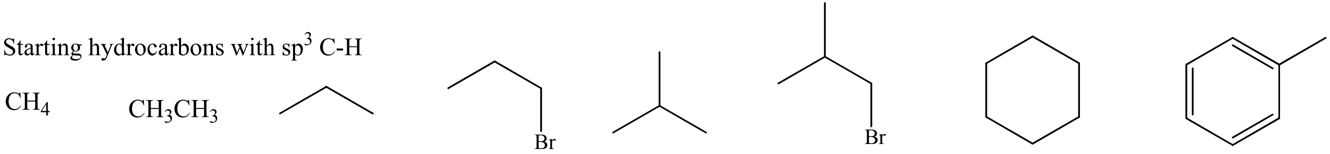
E or Z

other possible E products

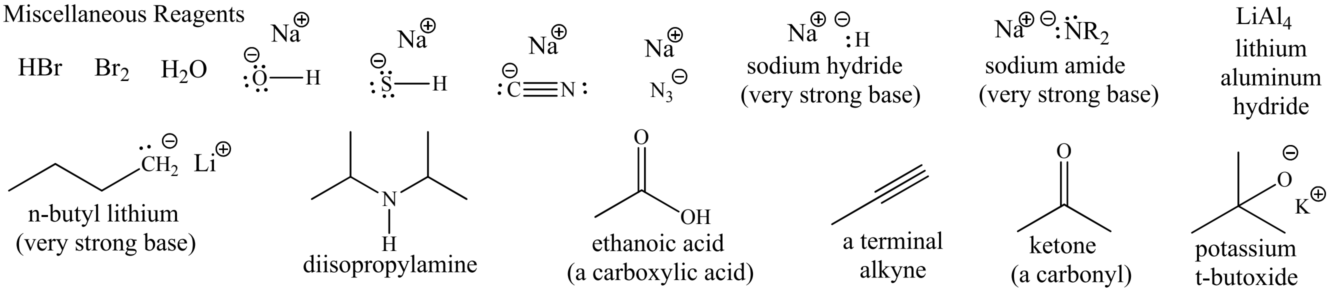
1 2 3 4 5

11. Propose a reasonable synthetic approach for 4 of the following molecules (a-f) starting from a given alkane. You may use any of the reagents available below. A molecule made in one part can be reused in another part without making it again. Just refer back to the part where it was made previously. (24 pts)

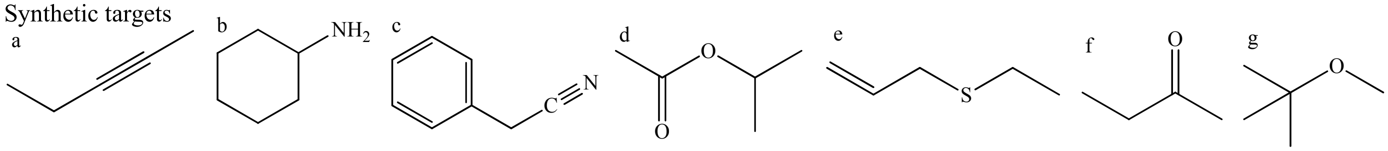
Starting hydrocarbons with sp^3 C-H



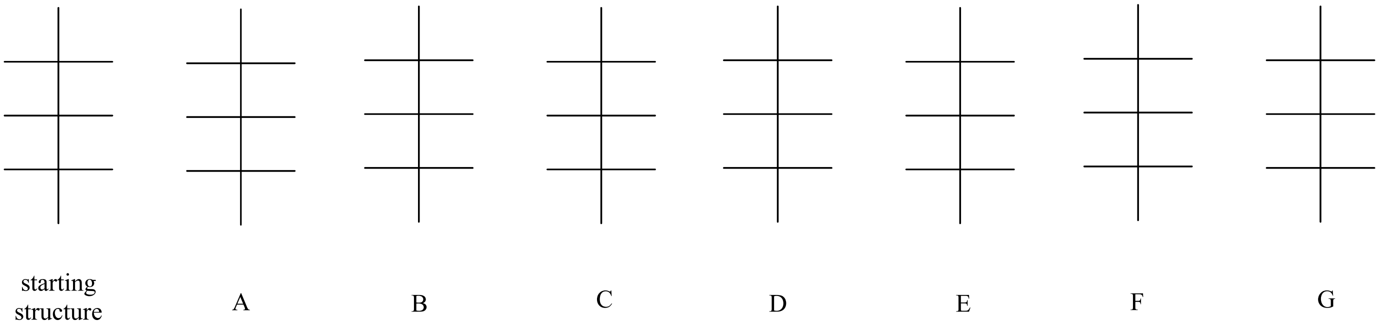
Miscellaneous Reagents



Synthetic targets



12. a. How many different types of sp^3 hydrogen atoms are present in 2S-bromo-3R-phenylpentane? Show all possible products when 2S-bromo-3R-phenylpentane 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, bromine substituted carbon = 800 and phenyl substituted carbon = 3000. (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 ΔH for each step of your mechanism using the given bond energies. (15 pts)

Br—Br	46
H—Br	87
CH_3-H	105
1° C-H	98
2° C-H	95
3° C-H	92
benzylic C-H	85
C_αBr-H	93
CH_3-Br	71
1° C-Br	69
2° C-Br	68
3° C-Br	66
benzylic C-Br	55
C_αBr-Br	67

Life is what we make it, always has been, always will be. ~Grandma Moses.

Typical Substitution Pattern Bond Energy Table (X-Y = bond) (* values in parentheses are estimated)

X \ Y =	H-	Me-	Et-	i-Pr	t-Bu	Ph	F-	Cl-	Br-	I-	RO-	H_2N-	N≡C−
CH_3- methyl	103	88	85	84	81	101	110	85	71	57	(96)	87	116
CH_3CH_2- primary	98	85	82	81	78	99	110	82	70	54	(92)	87	114
$(CH_3)_2CH$- secondary	95	84	81	79	74	97	109	81	69	54	(91)	86	112
$(CH_3)_3C$- tertiary	93	81	78	74	68	94	(108)	80	66	51	(90)	85	(111)
CH_2=$CHCH_2$- allyl	88	75	72	71	67	(87)	(96)	70	56	42	82	75	(104)
$C_6H_5CH_2$- benzyl	85	73	71	70	67	83	94	68	55	40	79	72	(100)
CH_2=CH- vinyl	110	98	95	93	89	108	(124)	92	79	(63)	not stable	not stable	128
C_6H_5- phenyl	111	101	97	95	92	110	124	95	80	64	111	104	128
CH_3CO- acyl	87	81	78	76	72	93	119	82	68	51	107	95	not common
CH_3CH_2O- alkoxy	104	(96)	(92)	(91)	(90)	101	low	low	low	low	40	low	low
H- hydrogen	119	103	98	95	93	111	135	103	88	71	111	93	125

Average Bond Energies (kcal/mole) (1 kcal = 4.184 joules)

	H	C	Si	N	O	S	F	Cl	Br	I	P
H	104	99	76	93	111	81	135	103	88	71	77
C		83	76	82	92	65	110	81	68	52	70
Si			53	85	108	70	135	91	74	56	76
N				40	48	X	65	46	X	X	X
O					40	X	45	52	48	48	80
S						60	68	61	52	X	X
F							37	X	X	65	117
Cl								58	X	50	78
Br									46	42	63
I										36	44
P											48

Multiple Bond Energies

C=C	146	C≡C	200
C=N	147	C≡N	213
C=O	179	C≡O	258
C=S	137	N≡N	226
N=N	109	P≡P	117
N=O	143		
P=O	130		
O=O	118		
S=O	128		
S=S	102		
P=P	84		