

**Organic Chemistry: Chem 210****Practice Exam 2A**

There are **31** questions on this exam. Check that you have done all of the problems and filled in the first **31** bubbles on the scantron. Most questions are worth 4 points; there are several two-point and one-point questions clearly labeled in the text. The maximum score on this exam is 100 points.

*Instructions***Answer sheet**

- 1) On the scantron, you need to clearly fill:
 - your **name** and your **student number**,
 - **section number**: (it is 001)
 - **test form** (white = test form A; yellow = test form B).
- 2) Use a #2 pencil

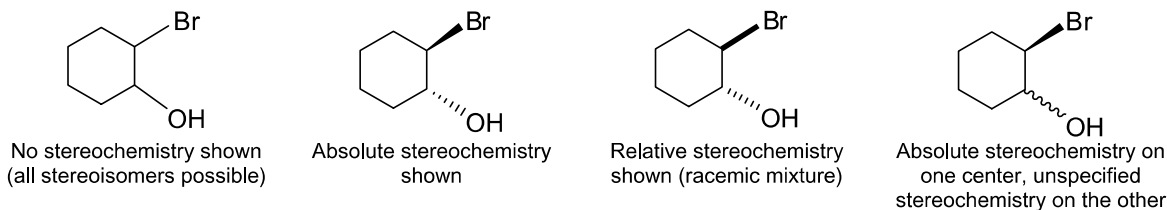
Exam policy

- 1) No electronic devices of any kind, such as calculators, cell phones, or even more advanced digital watches, are allowed. Possession of such devices during the exam, whether in use or not, is grounds for awarding a zero on the exam.
- 2) Molecular models are allowed (no instruction pages are permitted, however).
- 3) There are some blank pages at the end of the test that can be used as scratch paper.
- 4) Relevant tables, including the periodic table, are attached at the end of this exam.
- 5) Numerical values given in one question apply only to that question, and should not be used in other questions, unless there is a specific instruction to do so. If necessary, the values from the provided tables should be used, even if they differ from values that you may remember from different sources.
- 6) The exam results are based strictly on scantron's marks. No extraneous information is used to adjust the scores. Mark your choices with extra care.
- 7) Feel free to take this copy of the exam with you. The answer key will be posted on the web after the exam (under "News").

Hints

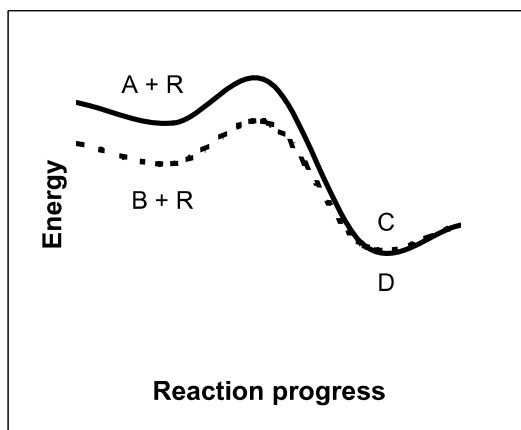
- 1) As you read the question, underline or circle key words to highlight them for yourself.
- 2) Questions have only one correct answer, unless indicated otherwise. No partial credit will be given.
- 3) There is no penalty for guessing.

Notes: I. The stereochemistry conventions are illustrated below:

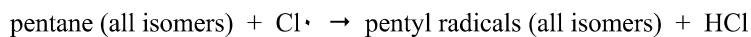


II. Abbreviations: Me = methyl, Et = ethyl, Pr = propyl, Bu = butyl, Pe = pentyl, Ph = phenyl (i.e. benzene as a substituent), AcO = acetate (H_3CCOO).

1. (4 pts) Consider the following reaction profiles where **A** reacts with reagent **R** and gets converted to **C**, and **B** reacts with the same reagent (**R**) under identical conditions and gets converted to **D**. Compounds **A** and **B** are stereoisomers of each other, and compounds **C** and **D** are stereoisomers of each other. Which statement about these compounds **must** be true?



- a) **A** and **B** are *E/Z* isomers
 b) **A** and **B** are diastereomers
 c) **C** and **D** are *meso* compounds
 d) **C** and **D** are constitutional isomers
2. (4 pts) A mixture of **all isomers** of pentane is allowed to react with chlorine radicals (produced by photochemical cleavage of Cl_2). How many different isomeric alkyl radicals (excluding stereoisomers) can form by hydrogen abstraction in the following reaction?



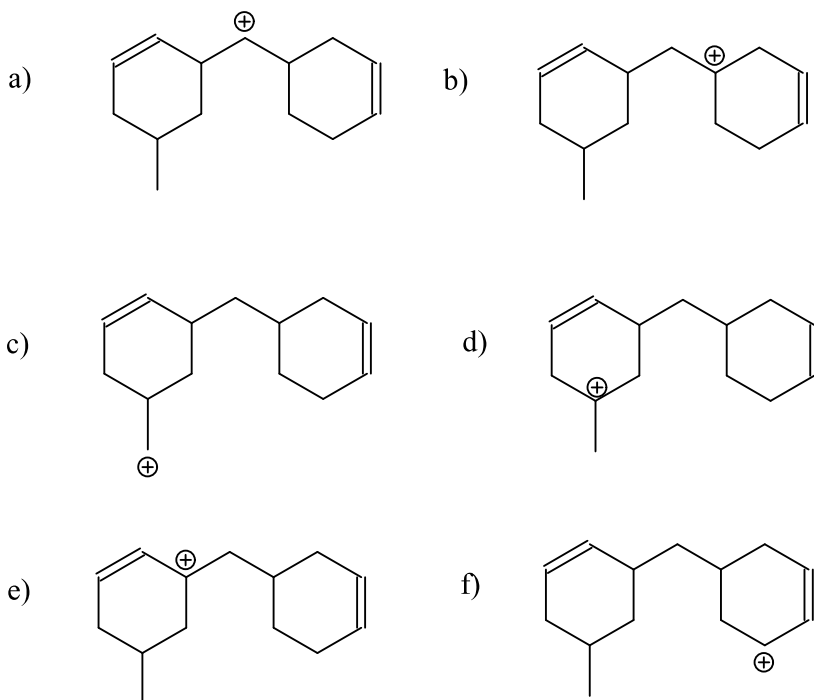
- a) 5 b) 6 c) 7 d) 8 e) 9

- 3-6. (1 pt each) Fill in the missing words in the passage below with words from the provided list to preserve best the meaning of the paragraph. Not all words have to be used. Some words may be used more than once.

“There are four general types of organic reactions. (3) reactions occur when two reactants combine to form a single new product. (4) occur when a single reactant splits into two products. (5) reactions occur when two reactants exchange parts to give two new products. (6) reactions occur when a single reactant undergoes a reorganization of bonds and atoms to yield an isomeric product.” (McMurry, J. *Organic Chemistry, 5th Ed.* Brooks/Cole, New York: 2000.)

- | | | |
|-----------------|------------------|------------------|
| a) Reduction | d) Addition | g) Transmutation |
| b) Substitution | e) Rearrangement | h) Reshuffling |
| c) Expulsion | f) Recombination | i) Elimination |

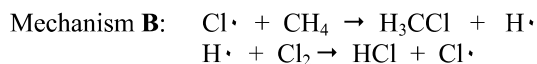
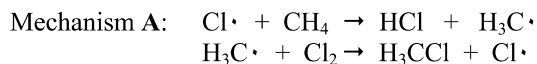
7. (4 pts) Which of the following is the most stabilized carbocation?



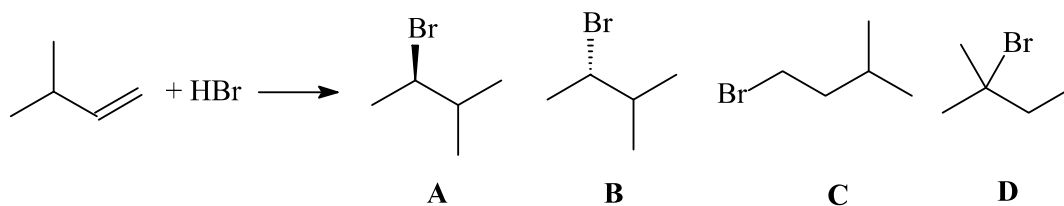
8. (4 pts) Which of the following **is not** a termination step in the chlorination reaction of methane?

- a) $\cdot\text{Cl} + \cdot\text{Cl} \rightarrow \text{Cl}_2$
 b) $\cdot\text{Cl} + \cdot\text{CH}_3 \rightarrow \text{CH}_3\text{Cl}$
 c) $\cdot\text{CH}_3 + \cdot\text{CH}_3 \rightarrow \text{C}_2\text{H}_6$
 d) $\cdot\text{Cl} + \text{Cl}_2 \rightarrow \text{Cl}_2 + \cdot\text{Cl}$
 e) $\cdot\text{Cl} + \cdot\text{CH}_2\text{Cl} \rightarrow \text{CH}_2\text{Cl}_2$

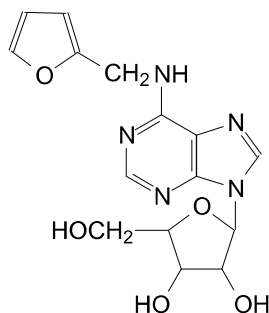
9. (4 pts) The chlorination of methane may proceed according to one of the two alternative mechanisms (only propagation steps are shown). Which statement about these alternative reactions is correct?



- a) Mechanism A is preferred because none of the steps is strongly endothermic.
 b) Mechanism A is preferred because the second step is strongly exothermic.
 c) Mechanism B is preferred because none of the steps is strongly endothermic.
 d) Mechanism B is preferred because the second step is strongly exothermic.
 e) Mechanisms A and B are equally likely, because they give the same net reaction.
10. (4 pts) Including a possibility of rearrangements, what is (are) the major organic product(s) of the following reaction?

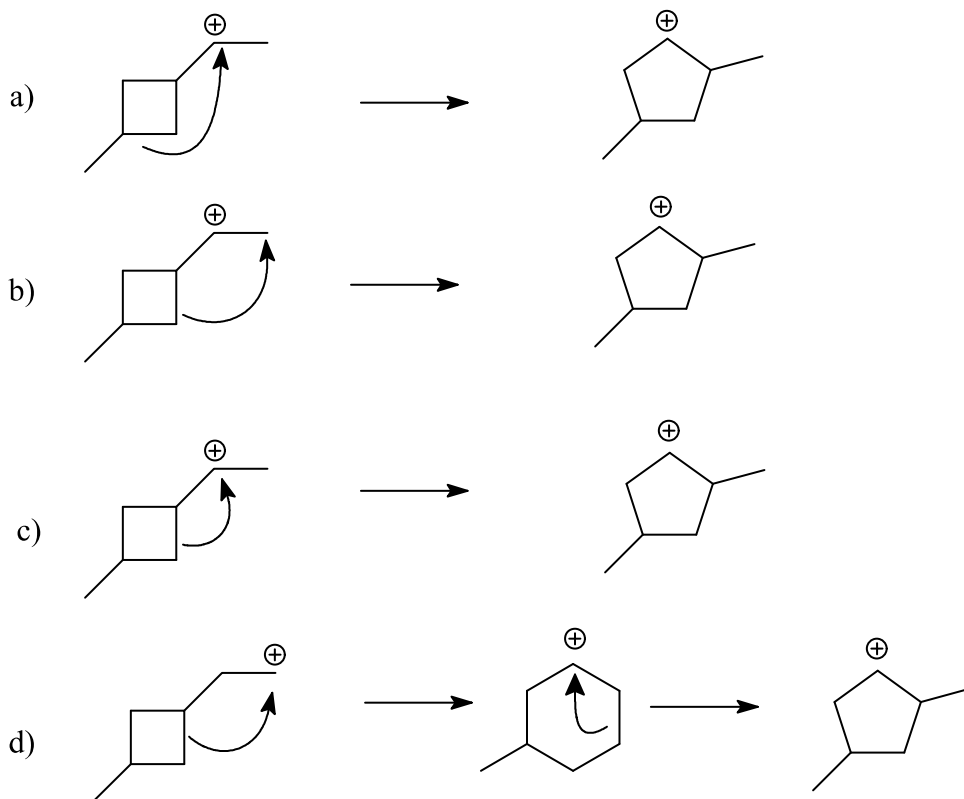
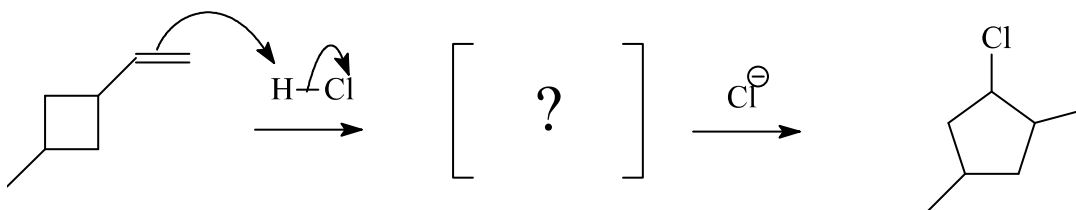


- a) A b) B c) C d) D e) A and B
 f) A and C g) C and D h) A, B, and D i) A, B, and C j) A, B, C, and D
11. (4 pts) Kinetin riboside is a modified nucleoside that is used to regulate growth in certain types of cell cultures. How many stereogenic **carbons** are in kinetin riboside (shown below)?

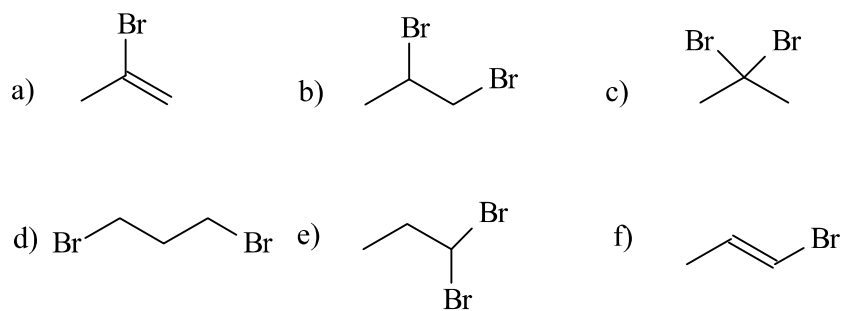


- a) 3 b) 4 c) 5 d) 6 e) 8

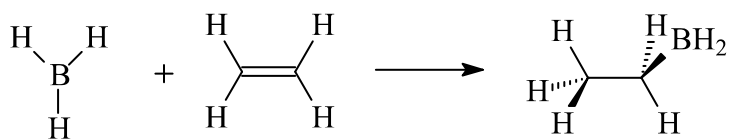
12. (4 pts) Which mechanism best accounts for the transformation in the brackets?



13. (4 pts) What is the major organic product of the following reaction?



14. (4 pts) Borane (BH_3) reacts as an electrophile with ethylene in an addition reaction. Taking into account the electronic structure of the reactants and the electronegativity of the atoms involved ($\text{C} = 2.5$, $\text{H} = 2.1$, $\text{B} = 2.0$), identify the critical HOMO and LUMO in the reactants.

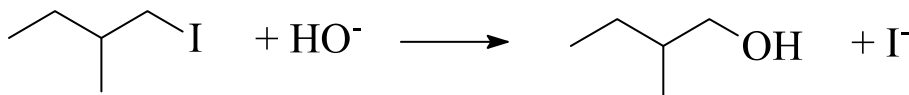
**HOMO**

- a) lone-pair on borane
- b) p orbital on borane
- c) sp^2 orbital on borane
- d) π orbital of ethylene
- e) π orbital of ethylene
- f) π orbital of ethylene

LUMO

- π^* of ethylene
- π of ethylene
- π^* of ethylene
- σ^* of borane
- s orbital of H^+
- p orbital on borane

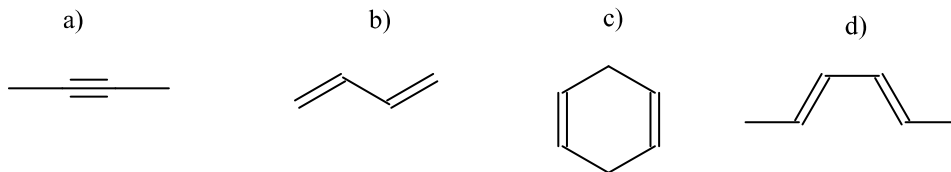
15. (2 pts) Consider the following back-side displacement reaction of (*S*)-(-)-1-iodo-2-methylbutane to produce (+)-2-methyl-1-butanol. What is the absolute configuration of the product?



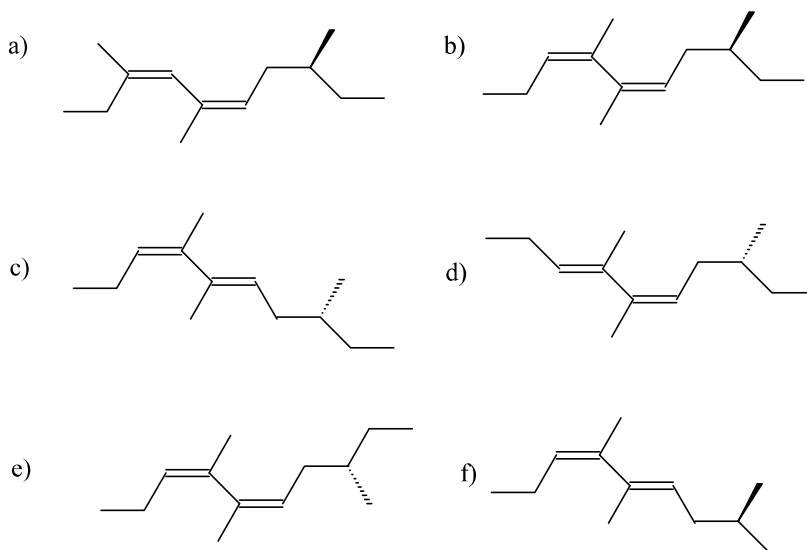
Note: Stereochemistry is not indicated in the reaction scheme.

- a) *R*
 - b) *S*
 - c) *R* and *S* (racemic mixture)
 - d) *R* and *S* (unequal amounts)
16. (4 pts) Molecules of compound **A** dissolved in hexane showed $[\alpha] = -23^\circ$. Which of the following conclusions **must be** correct?
- a) Compound **A** contains at least one chiral center.
 - b) Compound **A** cannot be a mixture of enantiomers.
 - c) Compound **A** has *S* absolute configuration.
 - d) Compound **A** is a diastereomer.
 - e) **A** and its mirror image are not superimposable.
 - f) **A** is a mixture of unequal amounts of two stereoisomers.

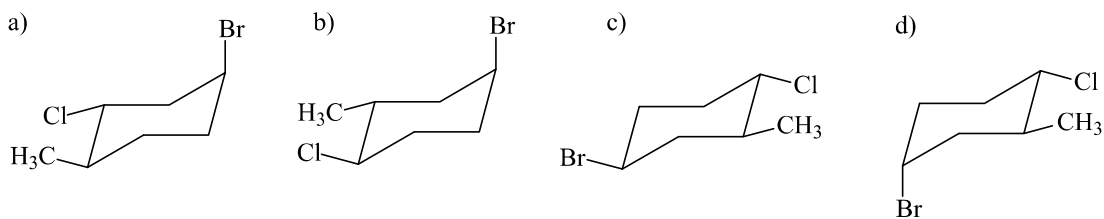
17. (4 pts) Each of the following compounds contains two π bonds. Which of these compounds will be most reactive in the electrophilic addition reaction with HBr ?



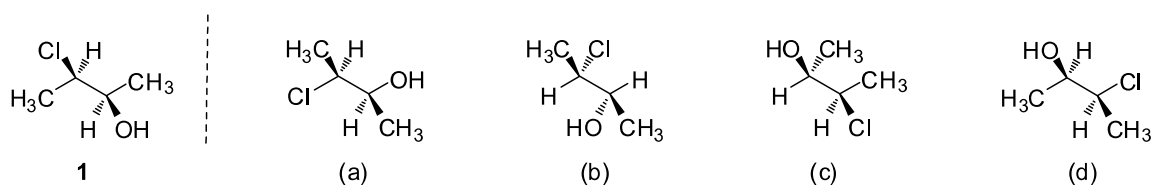
18. (4 pts) Which of the following represents the **mirror image** of (3*Z*, 5*E*, 8*S*)-4,5,8-trimethyl-3,5-decadiene?



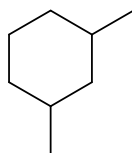
19. (4 pts) Which of the following structures represents the lowest-energy form of (1*S*, 2*S*, 4*R*)-4-bromo-1-chloro-2-methylcyclohexane?



20. (4 pts) Which compound is the enantiomer of **1**?

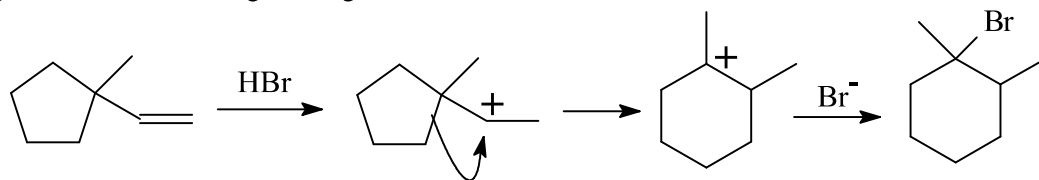


21. (4 pts) How many stereoisomers are possible for the following molecule?



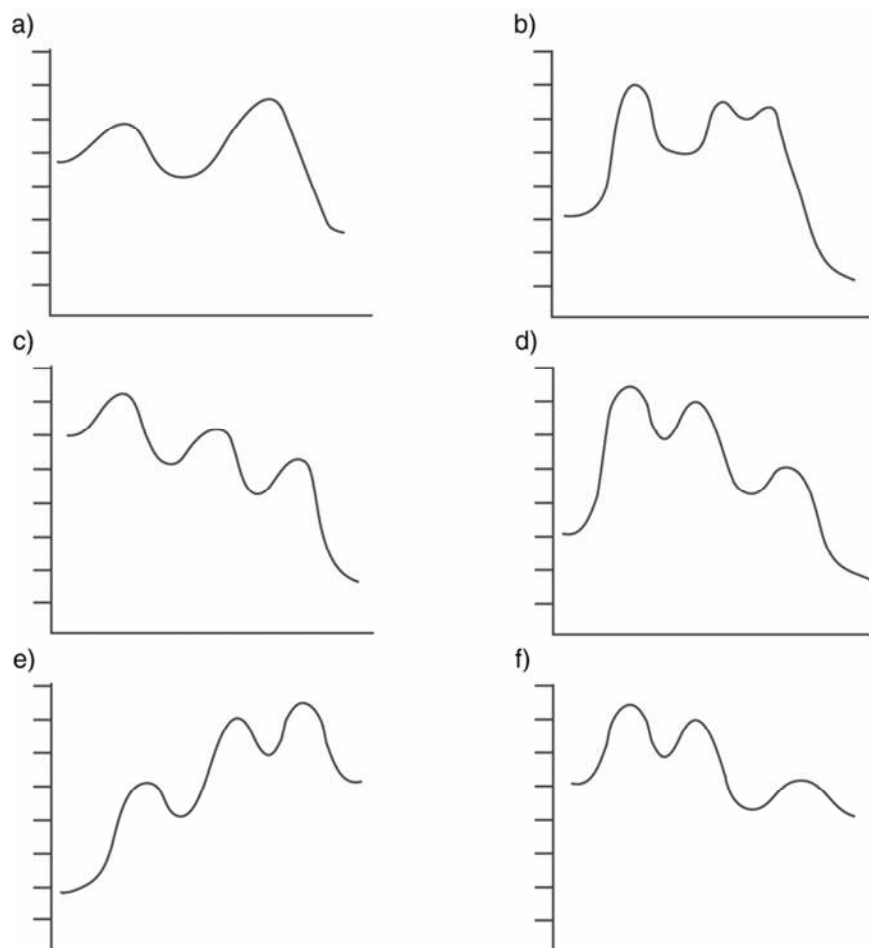
- a) 1 b) 2 c) 3 d) 4 e) 5

22. (4 pts) Consider the following rearrangement reaction:

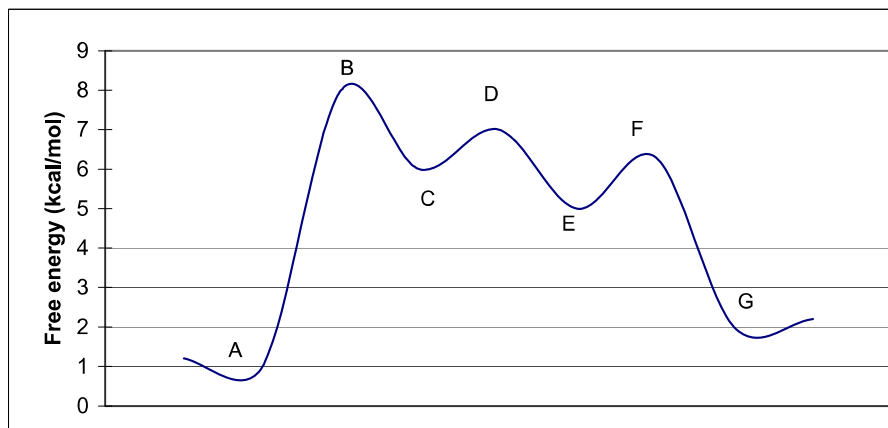


Which of the following reaction coordinates best represents the overall reaction?

(Note: the units are arbitrary)



23-27. (2 pts each) The free-energy profile for the transformation of **A** into **G** is shown below (the units are kcal/mol).



23. The overall reaction is:

- a) endergonic b) exergonic c) exocyclic d) exothermic e) epoxygonic

24. What is the slowest step in the forward direction?

- a) **A to C** b) **C to E** c) **E to G**

25. Which step in the **backward** direction releases the most free energy?

- a) **G to E** b) **E to C** c) **C to A**

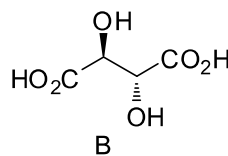
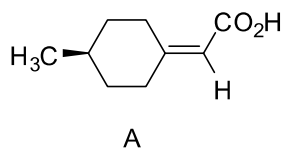
26. What is the fastest step in either direction?

- a) **A to C** b) **C to E** c) **E to G** d) **G to E** e) **E to C** f) **C to A**

27. What is the least stable transition state?

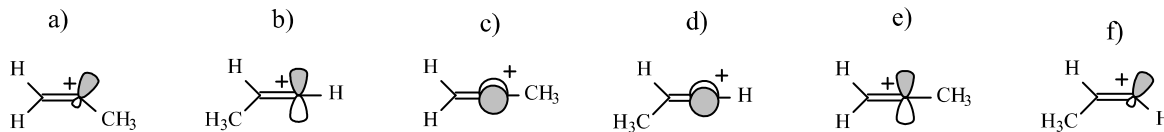
- a) **B** b) **C** c) **D** d) **E** e) **F**

28. (4 pts) Which of the following molecules is (are) chiral?



- a) **A** b) **B** c) both d) neither

29. (4 pts) What is the electronic structure of the cation formed by protonation of propyne ($\text{H}_3\text{CC}\equiv\text{CH}$)?

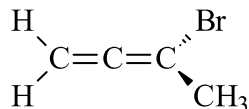


Note:  represents a view of a p orbital from the top



Note: In all drawings, all atoms (except for CH_3 hydrogens) are in the same plane.

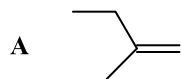
30. (4 pts) The compound shown below was synthesized by a Chem 213 student. By using a number of analytical techniques, she determined the structure. Her lab partner made a list of some of the expected properties of this molecule. Which of the listed properties is (are) correct?



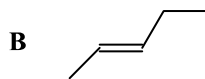
- A:** The molecule is chiral.
B: The molecule has 3 degrees of unsaturation.
C: The molecule has a conjugated π system.
D: If H^+ were to add to the central carbon, its hybridization would change from sp to sp^2 .
E: The molecule has a stereogenic center.

- a) **A** b) **B** c) **C** d) **D** e) **E**
 f) **A and B** g) **A and C** h) **A and D** i) **B and E** j) **C and D**

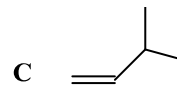
31. (4 pts) The heats of hydrogenation of three alkenes (**A**, **B**, and **C**) are given below in kcal/mol. Pentane is 2 kcal/mol less stable than 2-methylbutane. Arrange the three alkenes in order of their stability, starting with the most stable.



$$\Delta H_{\text{h}} = -28.0 \text{ kcal/mol}$$



$$\Delta H_{\text{h}} = -27.0 \text{ kcal/mol}$$



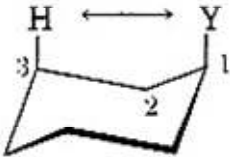
$$\Delta H_{\text{h}} = -30.0 \text{ kcal/mol}$$

- a) **A > B > C** b) **A > C > B** c) **B > A > C** d) **B > C > A** e) **C > B > A** f) **C > A > B**

end of the exam

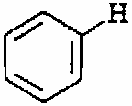
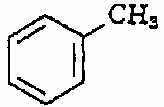
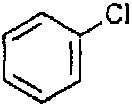
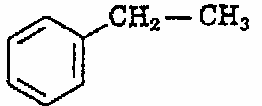
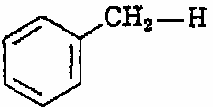
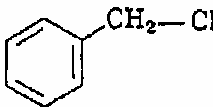
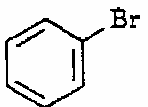
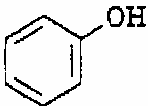
Total Strain Energies in Cycloalkanes			Energy Costs for Interactions in Alkane Conformers		
ring size	kJ/mol	kcal/mol	Interaction	kJ/mole	kcal/mole
3	115	27.6	H-H eclipsed	4.0	1.0
4	110	26.4	H-CH ₃ eclipsed	6.0	1.4
5	27	6.5	CH ₃ -CH ₃ eclipsed	11.0	2.6
6	0	0	CH ₃ -CH ₃ gauche	3.8	0.9
7	26	6.3			
8	40	8.6			

Steric Strain Due to 1,3-Diaxial Interactions

Y	Strain of one H-Y 1,3-diaxial interaction		
	(kcal/mol)	(kJ/mol)	
—F	0.12	0.5	
—Cl	0.25	1.0	
—Br	0.25	1.0	
—OH	0.5	2.1	
—CH ₃	0.9	3.8	
—CH ₂ CH ₃	0.95	4.0	
—CH(CH ₃) ₂	1.1	4.6	
—C(CH ₃) ₃	2.7	11.3	
—C ₆ H ₅	1.5	6.3	
—COOH	0.7	2.9	
—CN	0.1	0.4	

MAIN GROUPS												MAIN GROUPS							
1A		2A		TRANSITION METALS										3A	4A	5A	6A	7A	8A
1	2											13	14	15	16	17	18		
1 H 1.008												5 B 10.811	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.180		
3 Li 6.941	4 Be 9.012											13 Al 26.982	14 Si 28.086	15 P 30.974	16 S 32.066	17 Cl 35.453	18 Ar 39.948		
11 Na 22.990	12 Mg 24.305	3B 3	4B 4	5B 5	6B 6	7B 7	8B 8	8B 9	8B 10	1B 11	2B 12	31 Ga 69.723	32 Ge 72.61	33 As 74.992	34 Se 78.96	35 Br 79.904	36 Kr 83.80		
19 K 39.098	20 Ca 40.078	21 Sc 44.956	22 Ti 47.887	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.845	27 Co 58.933	28 Ni 58.693	29 Cu 63.546	30 Zn 65.39	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.29		
37 Rb 85.468	38 Sr 87.62	39 Y 88.906	40 Zr 91.224	41 Nb 92.906	42 Mo 95.94	43 Tc [98]	44 Ru 101.07	45 Rh 102.90	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po [209]	85 At [210]	86 Rn [222]		
55 Cs 132.91	56 Ba 137.33	57 La* 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59								
87 Fr [223]	88 Ra [226]	89 Ac** [227]	104 Rf [261]	105 Db [262]	106 Sg [266]	107 Bh [264]	108 Hs [265]	109 Mt [268]	110	111	112		114 [285]		116 [289]		118 [293]		
* LANTHANOIDS		58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm [145]	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.92	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97				
** ACTINOIDS		90 Th 232.04	91 Pa 321.04	92 U 238.03	93 Np [237]	94 Pu [244]	95 Am [243]	96 Cm [247]	97 Bk [247]	98 Cf [251]	99 Es [252]	100 Fm [257]	101 Md [258]	102 No [259]	103 Lr [262]				

TABLE 5.4 Bond Dissociation Energy Data for the Reaction $A-B \rightarrow A \cdot + B \cdot$

Bond	ΔH° (kcal/mol)	Bond	ΔH° (kcal/mol)	Bond	ΔH° (kcal/mol)
H—H	104	$(CH_3)_3C-I$	50	CH_3-CH_3	88
H—F	136	$H_2C=CH-H$	108	$C_2H_5-CH_3$	85
H—Cl	103	$H_2C=CH-Cl$	88	$(CH_3)_2CH-CH_3$	84
H—Br	88	$H_2C=CHCH_2-H$	87	$(CH_3)_3C-CH_3$	81
H—I	71	$H_2C=CHCH_2-Cl$	69	$H_2C=CH-CH_3$	97
Cl—Cl	58		112		102
Br—Br	46		97		72
I—I	36		85	$\begin{array}{c} O \\ \\ CH_3C-H \end{array}$	86
CH_3-H	104		70	HO—H	119
CH_3-Cl	84		82	HO—OH	51
CH_3-Br	70		112	CH_3O-H	102
CH_3-I	56	$HC\equiv C-H$	125	CH_3S-H	88
CH_3-OH	91	$HC\equiv CH$	210	C_2H_5O-H	103
CH_3-NH_2	80	$H_2C=CH_2$	150	$\begin{array}{c} O \\ \\ CH_3C-CH_3 \end{array}$	77
C_2H_5-H	98			$CH_3CH_2O-CH_3$	81
C_2H_5-Cl	81			NH_2-H	103
C_2H_5-Br	68			$H-CN$	130
C_2H_5-I	53				
C_2H_5-OH	91				
$(CH_3)_2CH-H$	95				
$(CH_3)_2CH-Cl$	80				
$(CH_3)_2CH-Br$	68				
$(CH_3)_3C-H$	91				
$(CH_3)_3C-Cl$	79				
$(CH_3)_3C-Br$	65				