



Organic Chemistry: Chem 210

Practice Exam 4A

There are **35** questions on this exam. The actual exam will be shorter (no more than 30 questions). Check that you have done all of the problems and filled in the first **35** bubbles on the scantron. Most questions are worth 4 points; there are several two-point questions clearly labeled in the text. The maximum score on this exam is 124 points (the actual exam will be worth 100 points).

Instructions

Answer sheet

- 1) On the scantron, you need to clearly fill:
 - your **name** and your **student number**,
 - **section number**
Section 001, 12:20 pm lecture
Section 002, 3:35 pm lecture
 - **test form** (white = test form A; yellow = test form B; blue = test form C, green = test form D).
- 2) Use a #2 pencil

Exam policy

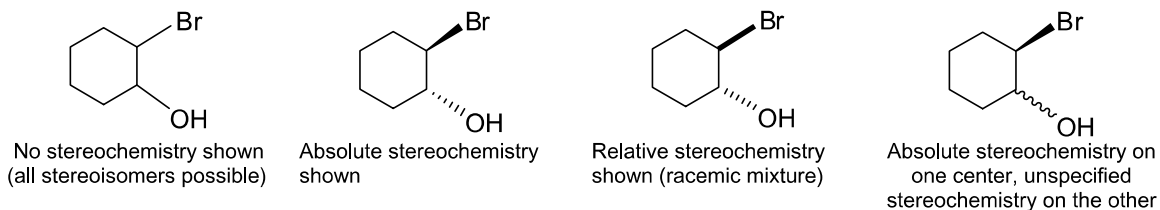
- 1) No electronic devices of any kind, such as calculators, cell phones, or even more advanced digital watches, are allowed. Possession of such devices during the exam, whether in use or not, is grounds for awarding a zero on the exam.
- 2) Molecular models are allowed (no instruction pages are permitted, 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) **You may not take the exam with you.** You may copy your answers on the provided page and compare them with the answer key. 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. No partial credit will be given.
- 3) There is no penalty for guessing.

Notes: I. When listing reagents, a slash (/) is used between reagents that are employed simultaneously, and a semicolon (;) is used between reagents that are employed in a stepwise fashion.

II. The stereochemistry conventions are illustrated below:



III. Abbreviations: Me = methyl, Et = ethyl, Pr = propyl, Bu = butyl, Pe = pentyl, Ph = phenyl (i.e. benzene as a substituent), AcO = acetate (H_3CCOO), MCPBA = m-chloroperbenzoic acid., TosO = TsO = tosylate

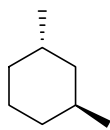
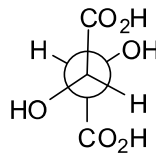
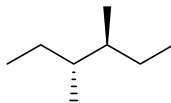
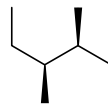
1. (4 pts) On Pluto, where everything is frozen, astronauts discovered two forms of **1,2-dibromoethane**: gauche and anti. Assuming that there are **no rotations** around single bonds, which statement about the two forms is correct?

- They are enantiomers.
- They are diastereoisomers.
- They are meso compounds.
- The gauche form has two stereogenic centers, and the anti has only one.
- Both will show optical activity.

2. (4 pts) What is the best description of the first organic intermediate formed when 2-butyne reacts with HCl?

- | | |
|-------------------|-------------------|
| a) allylic cation | d) vinylic cation |
| b) allylic anion | e) vinylic anion |
| c) chloronium ion | |

3. (4 pts) Which of the following will show optical activity?

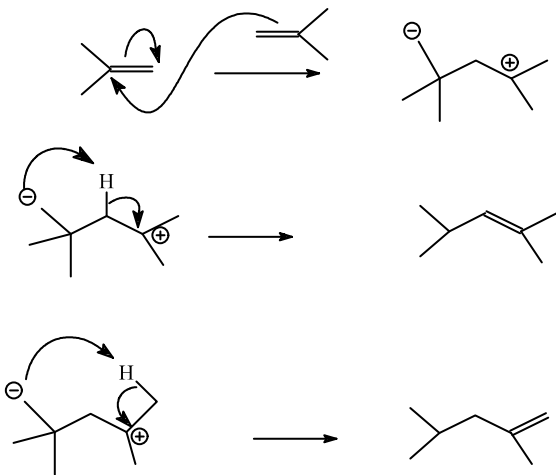
**A****B****C****D**

E: 50/50 mixture of **C** and **D**

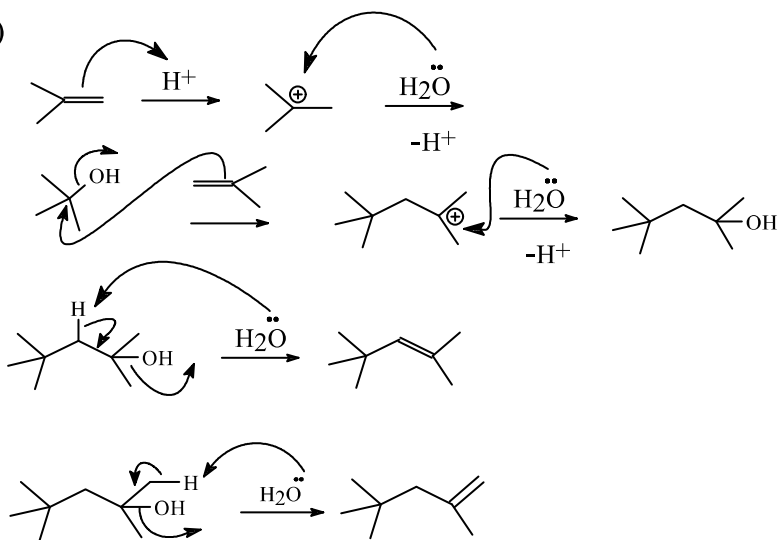
- a) **A, D, and E** d) **A and E** only
 b) **B, C, and D** e) All except **C**
 c) **B, C, and E**
4. (4 pts) One of the two chair conformations of *cis*-1-chloro-3-methylcyclohexane is more stable than the other by 3.70 kcal/mol. What is the energy cost of 1,3-diaxial interaction between a chlorine and a methyl group?
- a) 3.95 kcal/mol d) 3.05 kcal/mol
 b) 2.55 kcal/mol e) 4.85 kcal/mol
 c) 2.80 kcal/mol f) 3.70 kcal/mol

5. (4 pts) Heating of 2-methylpropene in 60% sulfuric acid gives a mixture of 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene. The best mechanism for these transformations is:

a)

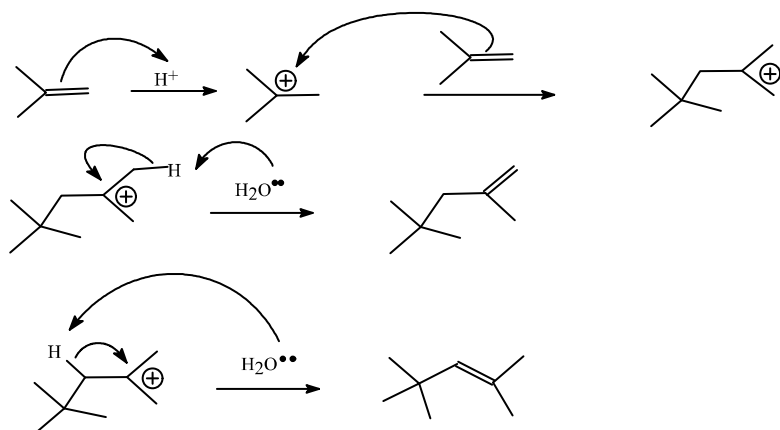


b)

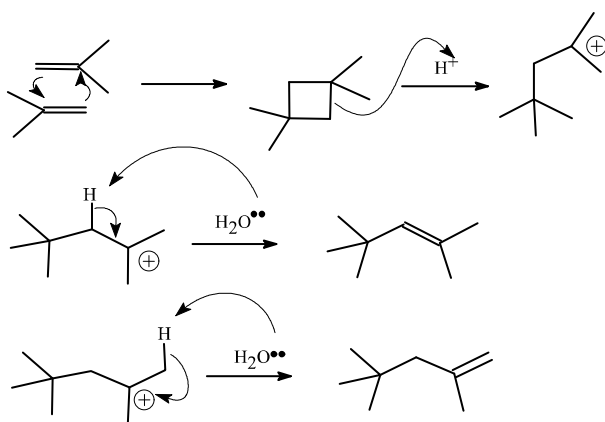


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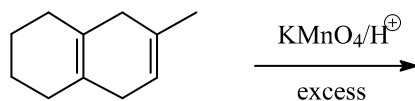
c)



d)

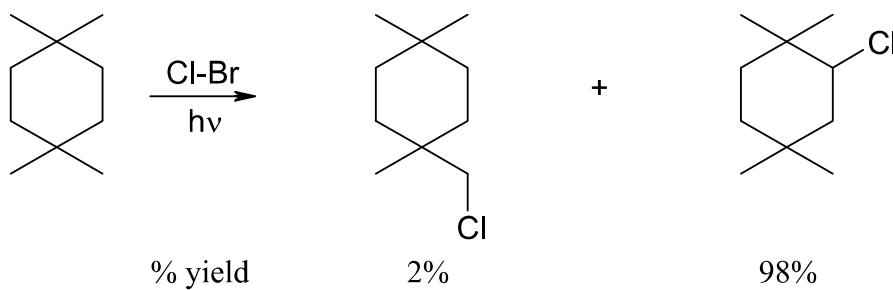


6. (4 pts) What is the final product of the following reaction?



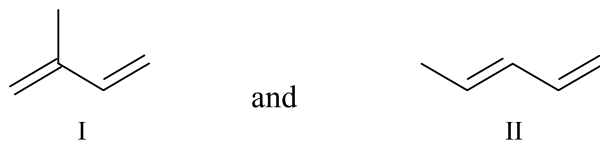
- a)
- b)
- c)
- d)

7. (4 pts) Which radical is responsible for the observed selectivity in the chain reaction below?

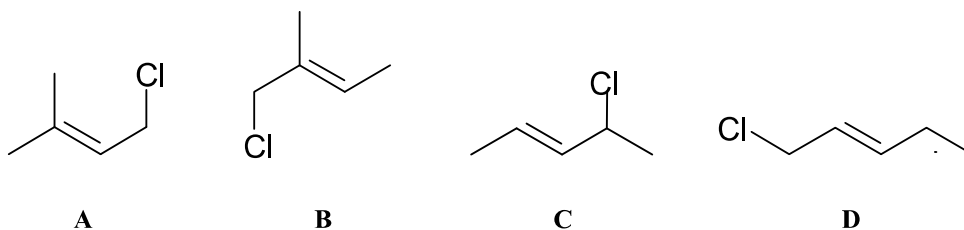


- a) $\text{Cl}\cdot$ b) $\text{Br}\cdot$ c) $\text{H}\cdot$ d) 1° alkyl radical e) 2° alkyl radical

8. (4 pts) Consider **1,4 - addition** of HCl to methyl-substituted butadienes:



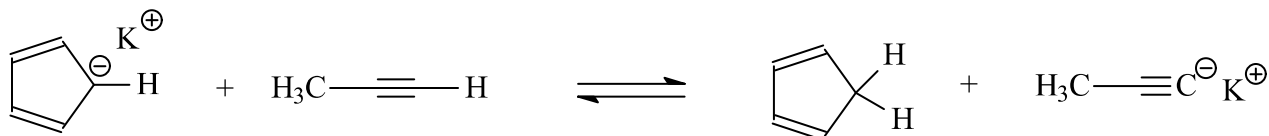
The possible 1,4 adducts are listed below:



Select **the major** 1,4-product for each diene:

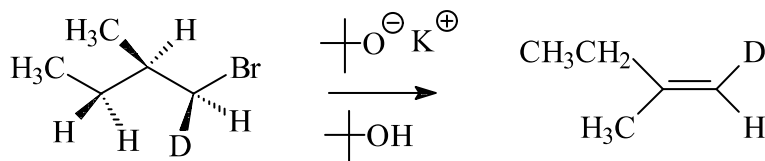
	<u>Diene I</u>	<u>Diene II</u>
a)	A	C
b)	A	D
c)	B	C
d)	B	D

9. (4 pts) What is true about the following equilibrium?



- It will be almost completely shifted to the left.
- It will be almost completely shifted to the right.
- The equilibrium constant is very close to one.
- The equilibrium constant is zero.

Questions **10** and **11** refer to the following reaction:



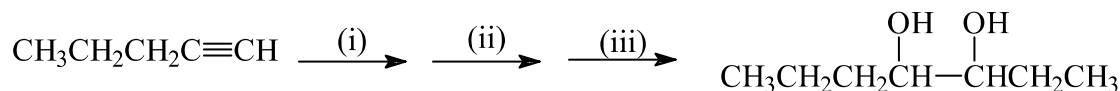
10. (4 pts) What is the mechanism of the above reaction?

- a) S_N1 d) E2
 b) S_N2 e) none of the above
 c) E1

11. (4 pts) What happens to the reaction rate if the concentration of t-butoxide is doubled?

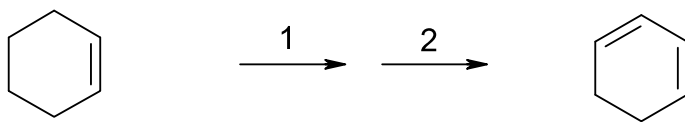
- a) no change d) tripled
 b) halved e) quadrupled
 c) doubled f) it depends on the extent of ion pair participation

12. (4 pts) For the following multistep synthesis, which set of reagents would be more likely to give the desired product?



- a) (i) HBr, (ii) O_3 followed by Zn/H^+ , (iii) Li/NH_3
 b) (i) $\text{NaNH}_2/\text{NH}_3$ followed by $\text{CH}_3\text{CH}_2\text{I}$ (ii) Lindlar's catalyst/ H_2
 (iii) OsO_4 followed by NaHSO_3
 c) (i) $\text{H}_2/\text{Pd}/\text{C}$ (1 equivalent), (ii) $\text{NaNH}_2/\text{NH}_3$ followed by $\text{CH}_3\text{CH}_2\text{Br}$,
 (iii) $\text{KMnO}_4/\text{OH}^-/\text{H}_2\text{O}$
 d) (i) $\text{HgSO}_4/\text{H}_2\text{O}/\text{H}_2\text{SO}_4$, (ii) Lindlar's catalyst/ H_2 , (iii) OsO_4
 followed by NaHSO_3

13. (4 pts) Consider the following transformation:



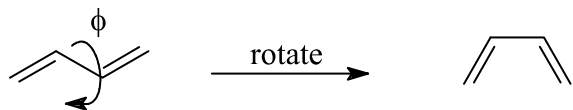
What reagents could be used to carry out this synthesis?

- | | <u>Step 1</u> | <u>Step 2</u> |
|----|-----------------------------------|--|
| a) | HBr/ether | NaNH ₂ /NH ₃ |
| b) | Br ₂ /CCl ₄ | NaOCH ₃ /CH ₃ OH |
| c) | NBS/hν | NaOH, heat |
| d) | NBS/DMSO/H ₂ O | PBr ₃ followed by HCl |
| e) | a and b would work | |
| f) | b and c would work | |
| g) | c and d would work | |

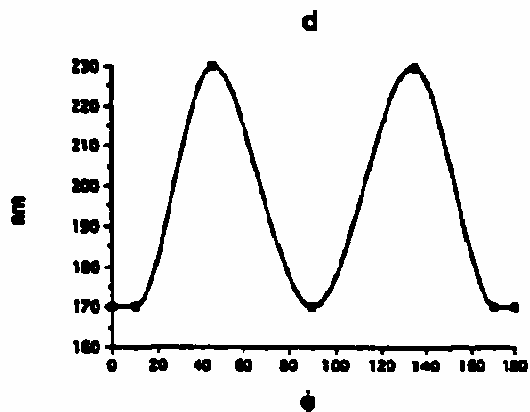
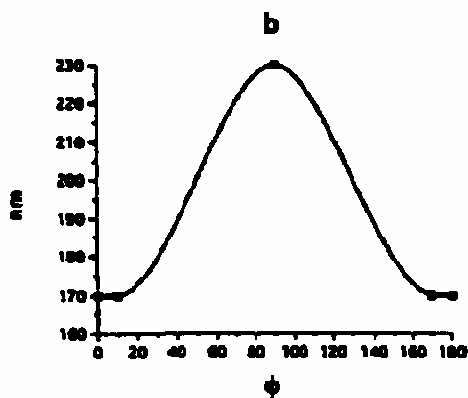
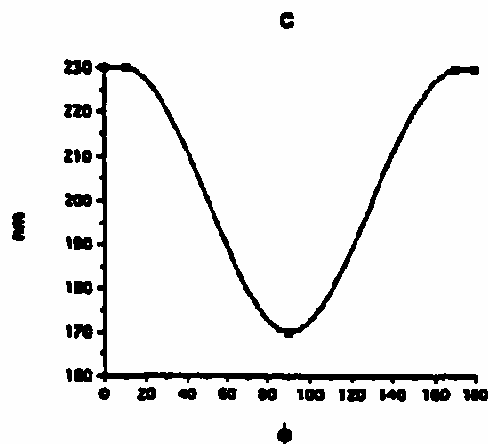
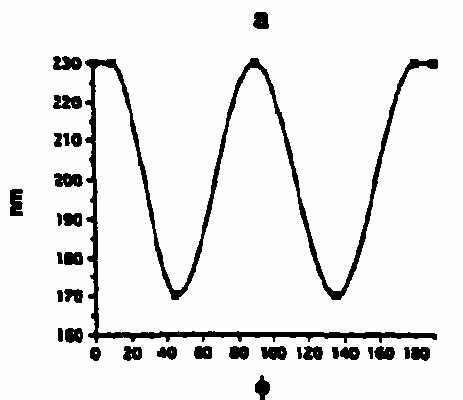
14. (4 pts) What is the product of dehydrohalogenation of (*R,R*)-2,3-dibromobutane?

- a)
- b)
- c)
- d)
- e)

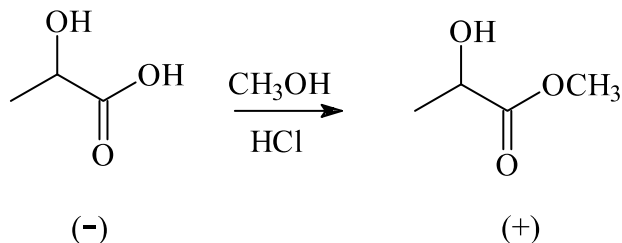
15. (4 pts) Consider the changes in the UV absorption of butadiene as it undergoes rotation about the central bond as shown (ϕ = angle of rotation).



Which graph best approximates the changes in the λ_{\max} as a function of ϕ .

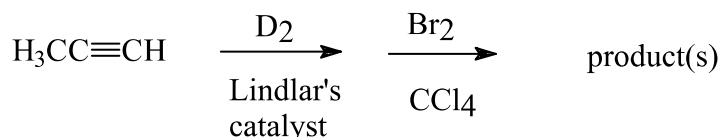


16. (4 pts) Esterification (shown below) is a reaction converting a carboxylic acid to its ester. It involves only the carbonyl carbon. Esterification of (-)-lactic acid with methanol yields (+)-methyl lactate. Assuming that there are no side reactions, what is true about this reaction?



- An S_N2 process has occurred, inverting the absolute configuration of the chiral center.
- An S_N1 reaction at the chiral center has inverted the optical rotation.
- A diastereomer has been produced; diastereomers have different physical properties, including optical rotation.
- Optical rotation is not directly related to absolute configuration, so the change in sign of rotation is merely a coincidence.

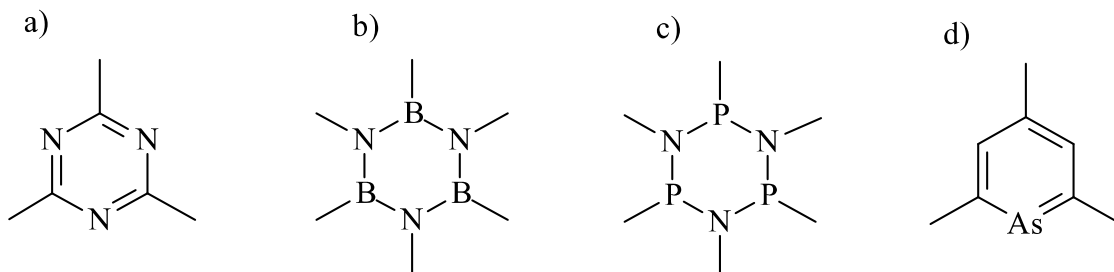
17. (4 pts) For the following series of reactions, what is the absolute configuration of the chiral centers in the major product(s)?



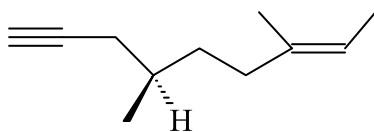
- $1S\ 2S$
 - $1R\ 2R$
 - $1R\ 2S$
 - $1S\ 2R$
 - 50% $1S\ 2R$ and 50% $1R\ 2S$
 - 50% $1S\ 2S$ and 50% $1R\ 2S$
18. (4 pts) Which of the following statements about the reactivity-selectivity principle is correct?

- Intermediates involved in exergonic reactions are more selective than the same intermediates involved in endergonic reactions.
- Intermediates involved in exergonic reactions have later transition states than the same intermediates involved in endergonic reactions.
- Intermediates involved in exergonic reactions are less reactive than the same intermediates involved in endergonic reactions.
- Intermediates involved in exergonic reactions are less selective than the same intermediates involved in endergonic reactions.

19. (4 pts) Which of the following heterocycles **is not** aromatic? Note that lone electron pairs are not shown explicitly.



20. (4 pts) Which is the best IUPAC name for the following structure?



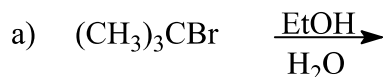
- a) (*S*)-*E*-3,6-dimethyl-8-nonyn-2-ene
 b) (*R*)-*E*-4,7-dimethyl-7-nonen-1-yne
 c) (*R*)-*E*-3,6-dimethyl-8-nonyl-1-ene
 d) (*S*)-*Z*-4,7-dimethyl-7-nonen-1-yne
 e) (*R*)-*Z*-4,7-dimethylnonan-7-en-1-yne

21. (4 pts) Which of the following compounds is most stable?

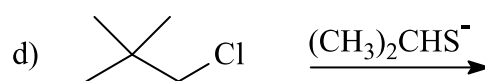
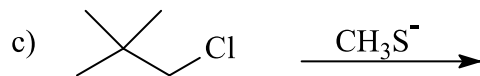
- a) (1*S*, 3*R*)-1-*t*-butyl-3-methylcyclohexane
 b) (1*S*, 3*S*)- 1-*t*-butyl-3-methylcyclohexane
 c) *trans*- 1-*t*-butyl-3-methylcyclohexane
 d) (1*R*, 3*R*)- 1-*t*-butyl-3-methylcyclohexane

22-25 (2 points each) Which reaction in each pair shown below will show the faster rate of disappearance (consumption) of substrate (starting material)?

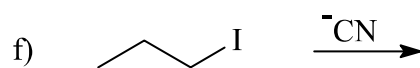
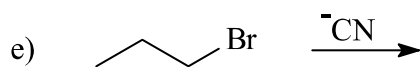
22. (2 pts)



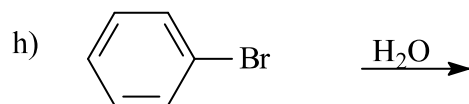
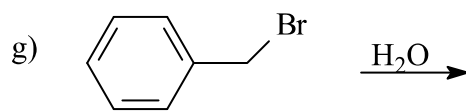
23. (2 pts)



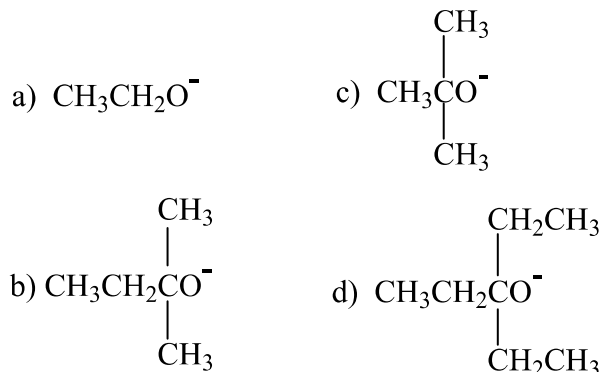
24. (2 pts)



25. (2 pts)



26 and 27. (2 points each) When 2-bromo-2,3-dimethylbutane reacts with any of the bases shown below under E2 conditions, two alkenes are produced: 2,3-dimethyl-1-butene and 2,3-dimethyl-2-butene.



26. (2 pts) Which one of the bases shown above would produce the highest yield of 2,3-dimethyl-1-butene?

27. (2 pts) Which one of the bases shown above would produce the highest yield of 2,3-dimethyl-2-butene?

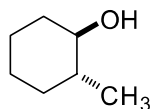
28 and 29. (2 pts each) Fill in the blanks with one of the orbitals listed below to provide the best (most precise) meaning to the following two sentences.

From Streitwieser, Heathcock, and Kosower, 4th edition:

“In an $\text{S}_{\text{N}}2$ reaction the donor is the entering nucleophile whose HOMO is a 28. The acceptor is the organic substrate whose LUMO for the reaction is a 29 involving the leaving group.”

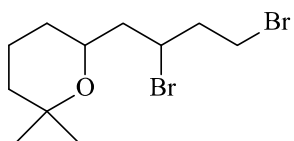
- a) σ orbital
- b) σ^* orbital
- c) π orbital
- d) π^* orbital
- e) lone-pair orbital

30. (4 pts) Select the **best** method for preparation of the following compound:

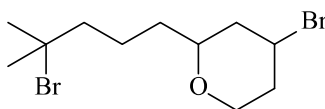


- react cyclohexanone with CH_3Li
- react 1-methylcyclohexene with $\text{Hg}(\text{OAc})_2$ followed by NaBH_4
- react cyclohexene with BH_3 ; $\text{NaOH}/\text{H}_2\text{O}_2$, followed by CH_3Br
- react cyclohexene with MCPBA, followed by CH_3MgBr
- react 1-methylcyclohexene with $\text{KMnO}_4/\text{NaOH}$

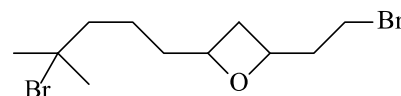
31. (4 pts) When 1,3,9-tribromo-9-methyl-5-decanol is treated with base it can form three cyclic ethers by an $\text{S}_{\text{N}}2$ reaction. Which one will form fastest?



a)



b)

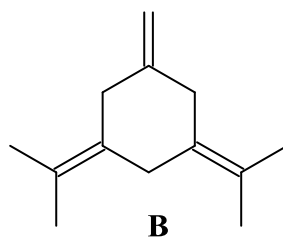


c)

32. (4 pts) Which is the **best** sequence of reactions for preparation of 2,4-dinitrobenzoic acid from benzene?

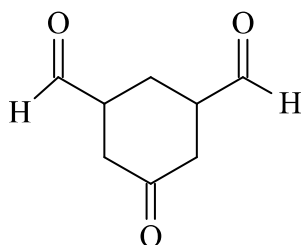
1. $\text{HNO}_3/\text{H}_2\text{SO}_4$ 2. $\text{CH}_3\text{Br}/\text{AlCl}_3$ 3. $\text{HNO}_3/\text{H}_2\text{SO}_4$ 4. KMnO_4/H^+
1. $\text{CH}_3\text{Br}/\text{AlCl}_3$ 2. $\text{HNO}_3/\text{H}_2\text{SO}_4$ 3. KMnO_4/H^+ 4. $\text{HNO}_3/\text{H}_2\text{SO}_4$
1. $\text{CH}_3\text{Br}/\text{AlCl}_3$ 2. KMnO_4/H^+ 3. $\text{HNO}_3/\text{H}_2\text{SO}_4$ (excess)
1. $\text{HNO}_3/\text{H}_2\text{SO}_4$ 2. $\text{CH}_3\text{Br}/\text{AlCl}_3$ 3. KMnO_4/H^+ 4. $\text{HNO}_3/\text{H}_2\text{SO}_4$
1. $\text{CH}_3\text{Br}/\text{AlCl}_3$ 2. $\text{HNO}_3/\text{H}_2\text{SO}_4$ (excess) 3. KMnO_4/H^+

33. (4 pts) Compound **A** was treated with a large excess of CH_3MgBr . The resulting product was exposed to $\text{POCl}_3/\text{pyridine}$ to give compound **B**, as one of many products.

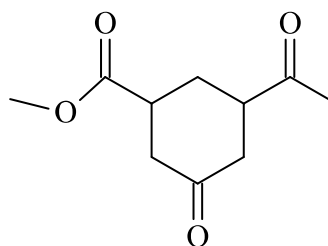


Which of the following compounds can be **A**?

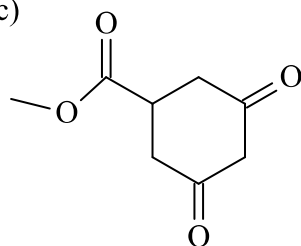
a)



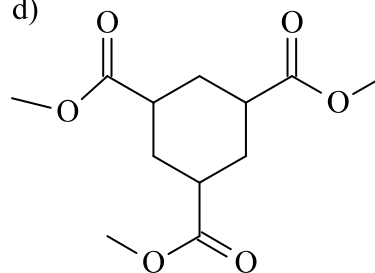
b)



c)



d)

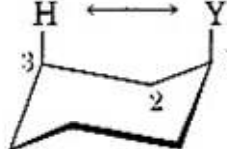


34. (4 pts) Oxidation of 1° alcohols with CrO₃/H₂SO₄/H₂O/acetone produces carboxylic acids. Oxidation of 1° alcohols with pyridinium chlorochromate in a dry solvent (e.g., CH₂Cl₂) produces an aldehyde. Which of the following is true?
- a) The initial product of oxidation is always the carboxylic acid when using CrO₃/H₂SO₄/H₂O/acetone.
 - b) The initially formed product of CrO₃/H₂SO₄/H₂O/acetone oxidation can undergo a second E2-like elimination of the chromate derived from the hydrated aldehyde.
 - c) Pyridinium chlorochromate oxidations always stop at the aldehyde, regardless of conditions.
 - d) Pyridinium chlorochromate in an anhydrous solvent prevents the aldehyde from forming the hydrate. Therefore, further oxidation cannot take place.
 - e) a and c
 - f) b and c
 - g) b and d
35. (4 pts) Which of the following series of reactions is the **best** way to convert **R**-2-pentanol to **R**-2-ethoxypentane?
- a) *p*-TosCl/pyridine; EtOH/NaOH
 - b) *p*-TosCl/pyridine; PBr₃/ether; NaOEt/EtOH
 - c) PBr₃/ether; NaOEt/DMSO
 - d) EtOH/NaOH; HCl
 - e) HBr; NaOEt/EtOH

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	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18																																																						
1 H 1.008	2 Li 6.941	3 Be 9.012	4 Na 22.990	5 Mg 24.305	6 Sc 44.956	7 Ti 47.887	8 V 50.942	9 Cr 51.996	10 Mn 54.938	11 Fe 55.845	12 Co 58.933	13 Ni 58.693	14 Cu 63.546	15 Zn 65.39	16 Ga 69.723	17 Ge 72.61	18 As 74.992	19 Se 78.96	20 Br 79.904	21 Kr 83.80	22 Rb 85.468	23 Sr 87.62	24 Y 88.906	25 Zr 91.224	26 Nb 92.906	27 Mo 95.94	28 Tc 98	29 Ru 101.07	30 Rh 102.90	31 Pd 106.42	32 Ag 107.87	33 Cd 112.41	34 In 114.82	35 Sn 118.71	36 Sb 121.76	37 Te 127.60	38 I 126.90	39 Xe 131.29	40 Cs 132.91	41 Ba 137.33	42 La* 138.91	43 Hf 178.49	44 Ta 180.95	45 W 183.84	46 Re 186.21	47 Os 190.23	48 Ir 192.22	49 Pt 195.08	50 Au 196.97	51 Hg 200.59	52 Tl 204.38	53 Pb 207.2	54 Bi 208.98	55 Po [209]	56 At [210]	57 Rn [222]	58 Fr [223]	59 Ra [226]	60 Ac** [227]	61 Rf [261]	62 Db [262]	63 Sg [266]	64 Bh [264]	65 Hs [265]	66 Mt [268]	67 110	68 111	69 112	70 114	71 116	72 118
* 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]																																																							

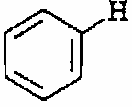
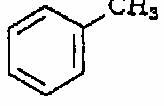
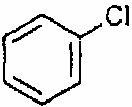
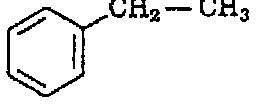
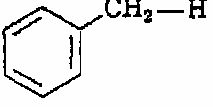
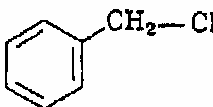
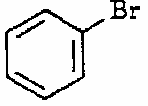
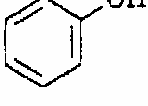
TABLE 22.1 Acidity Constants for Some Organic Compounds

Compound type	Compound	pK _a
Carboxylic acid	CH ₃ COOH	5
1,3-Diketone	CH ₂ (COCH ₃) ₂	9
1,3-Keto ester	CH ₂ COCH ₂ CO ₂ C ₂ H ₅	11
1,3-Dinitrile	CH ₂ (CN) ₂	11
1,3-Diester	CH ₂ (CO ₂ C ₂ H ₅) ₂	13
Water	HOH	16
Primary alcohol	CH ₃ CH ₂ OH	16
Acid chloride	CH ₃ COCl	16
Aldehyde	CH ₃ CHO	17
Ketone	CH ₃ COCH ₃	19
Ester	CH ₃ CO ₂ C ₂ H ₅	25
Nitrile	CH ₃ CN	25
Dialkylamide	CH ₃ CON(CH ₃) ₂	30
Ammonia	NH ₃	35
Dialkylamine	HN(<i>i</i> -C ₃ H ₇) ₂	40
Alkyne	HC≡CH	25
Alkene	CH ₂ =CH ₂	49
Alkane	CH ₃ Cl ₃	60

Selectivity of halogen radicals (per H)

	3°	2°	1°
F·	2	1	1
Cl·	5	3.5	1
Br·	1600	80	1
I·	97000	1100	1

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	$CH_3C(=O)-H$	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	$CH_3C(=O)-CH_3$	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				