

CHEM 3311 (Richardson) Third Hour Exam – April 14, 2015

Your Name _____

Key

Student ID _____

Recitation Time 12:00 Monday, 1:00 Monday,
11:00 Tuesday, 1:00 Tuesday,
12:00 Wednesday

Question	Score	Out of
1		20
2		12
3		16
4		12
5		10
6		15
7		15
8		5 e.c.
Total		100

This is a closed-book exam. The use of notes, calculators, or cell phones will not be allowed during the exam. You may use models sets brought in a clear ziplock bag. Use the backs of the pages for scratch work. If your final answer is not clearly specified, you will lose points. For mechanisms, show all intermediates including correct formal charges, but do not show transition states.

hydrogen 1 H 1.0079																	helium 2 He 4.0026						
lithium 3 Li 6.941	beryllium 4 Be 9.0122																	boron 5 B 10.811	carbon 6 C 12.011	nitrogen 7 N 14.007	oxygen 8 O 15.999	fluorine 9 F 18.998	neon 10 Ne 20.180
sodium 11 Na 22.990	magnesium 12 Mg 24.305																	aluminum 13 Al 26.982	silicon 14 Si 28.086	phosphorus 15 P 30.974	sulfur 16 S 32.065	chlorine 17 Cl 35.453	argon 18 Ar 39.948
potassium 19 K 39.098	calcium 20 Ca 40.078	scandium 21 Sc 44.956	titanium 22 Ti 47.867	vanadium 23 V 50.942	chromium 24 Cr 51.996	manganese 25 Mn 54.938	iron 26 Fe 55.845	cobalt 27 Co 58.933	nickel 28 Ni 58.693	copper 29 Cu 63.546	zinc 30 Zn 65.38	gallium 31 Ga 69.723	germanium 32 Ge 72.64	arsenic 33 As 74.922	selenium 34 Se 78.96	bromine 35 Br 79.904	krypton 36 Kr 83.80						
rubidium 37 Rb 85.468	strontium 38 Sr 87.62	yttrium 39 Y 88.906	zirconium 40 Zr 91.224	niobium 41 Nb 92.906	molybdenum 42 Mo 95.94	technetium 43 Tc 98	ruthenium 44 Ru 101.07	rhodium 45 Rh 103.91	palladium 46 Pd 106.42	silver 47 Ag 107.87	cadmium 48 Cd 112.41	indium 49 In 114.82	tin 50 Sn 118.71	antimony 51 Sb 121.76	tellurium 52 Te 127.60	iodine 53 I 126.90	xenon 54 Xe 131.29						
cesium 55 Cs 132.91	barium 56 Ba 137.33	* 57-70	lanthanum 57 La 138.91	cerium 58 Ce 140.12	praseodymium 59 Pr 140.91	neodymium 60 Nd 144.24	promethium 61 Pm 144.91	samarium 62 Sm 150.36	europtium 63 Eu 151.96	gadolinium 64 Gd 157.25	terbium 65 Tb 158.93	dysprosium 66 Dy 162.50	holmium 67 Ho 164.93	erbium 68 Er 167.26	thulium 69 Tm 168.93	ytterbium 70 Yb 173.04	radium 88 Ra 226						
francium 87 Fr [223]	radium 88 Ra [226]	* * *	actinium 89 Ac [227]	thorium 90 Th 232.04	protactinium 91 Pa 231.04	uranium 92 U 238.03	neptunium 93 Np [237]	plutonium 94 Pu [244]	americium 95 Am [243]	curium 96 Cm [247]	berkelium 97 Bk [247]	californium 98 Cf [251]	einsteinium 99 Es [252]	fermium 100 Fm [257]	mendelevium 101 Md [258]	nobelium 102 No [259]	roentgenium 111 Rg [272]	copernicium 112 Cn [285]					

* Lanthanide series

* * Actinide series

lanthanum 57 La	cerium 58 Ce	praseodymium 59 Pr	neodymium 60 Nd	promethium 61 Pm	samarium 62 Sm	europtium 63 Eu	gadolinium 64 Gd	terbium 65 Tb	dysprosium 66 Dy	holmium 67 Ho	erbium 68 Er	thulium 69 Tm	ytterbium 70 Yb
138.91	140.12	140.91	144.24	144.91	150.36	151.96	157.25	158.93	162.50	164.93	167.26	168.93	173.04
actinium 89 Ac	thorium 90 Th	protactinium 91 Pa	uranium 92 U	neptunium 93 Np	plutonium 94 Pu	americium 95 Am	curium 96 Cm	berkelium 97 Bk	californium 98 Cf	einsteinium 99 Es	fermium 100 Fm	mendelevium 101 Md	nobelium 102 No
[227]	232.04	231.04	238.03	[237]	[244]	[243]	[247]	[247]	[251]	[252]	[257]	[258]	[259]

pKa Values

HI	-10	CH ₃ COOH	4.7	Phenol	10	H ₂	35
HBr	-8	HN ₃	4.7	RSH	10-12	NH ₃	36
HCl	-6	H ₂ S	7.0	H ₂ O	15.7	H ₂ C=CH ₂	45
H ₃ O ⁺	-1.7	NH ₄ ⁺	9.3	Alcohol (ROH)	16-18	CH ₄	60
HF	3.2	HCN	9.4	HC≡CH	26		

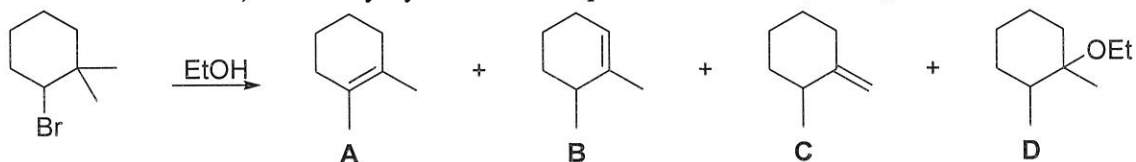
Average: 72.5

St. Dev: 16.0

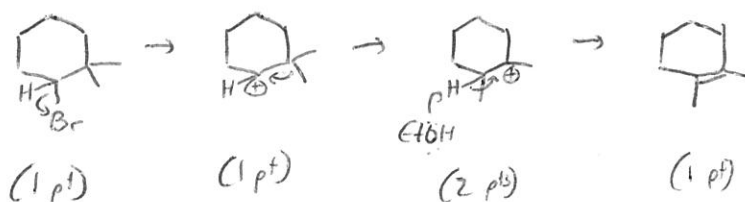
Max: 98

Min: 24

- 1) When 2-bromo-1,1-dimethylcyclohexane is placed in ethanol, four products are observed.

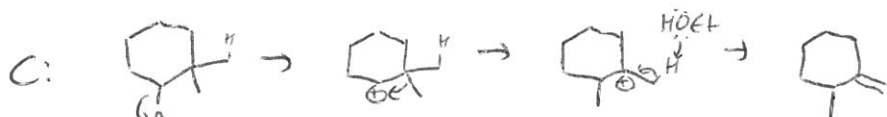
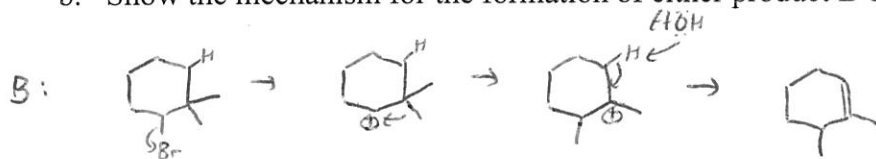


- a. Show the mechanism for the formation of product A. (5 pts)

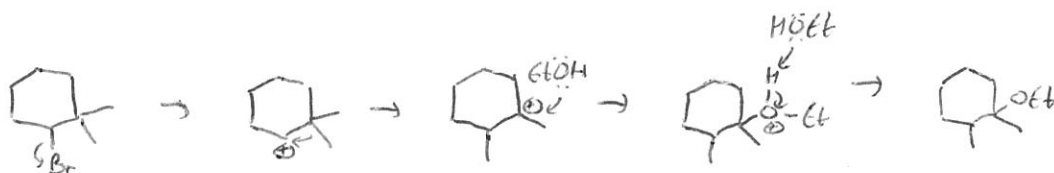


-2 pts for not using EtOH to deprotonate
-3 pts if EtO⁻ shows up

- b. Show the mechanism for the formation of either product B or C (your choice). (5 pts)



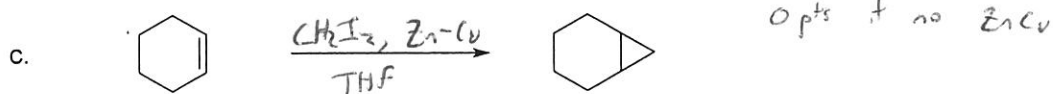
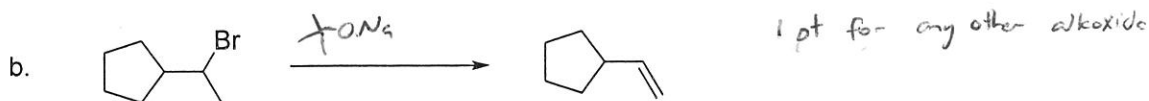
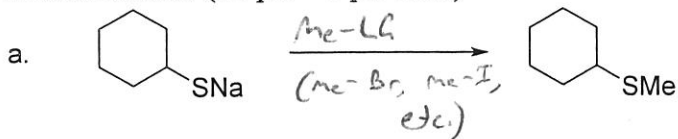
- c. Show the mechanism for the formation of product D. (5 pts)



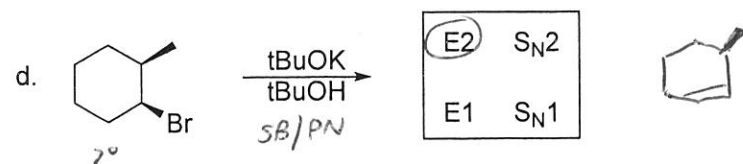
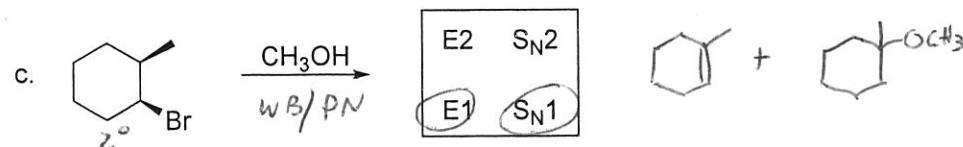
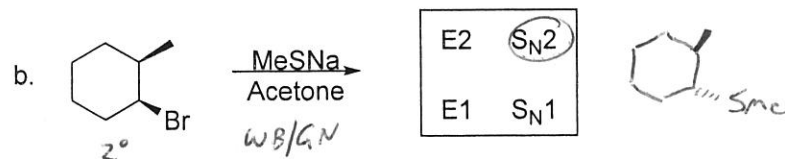
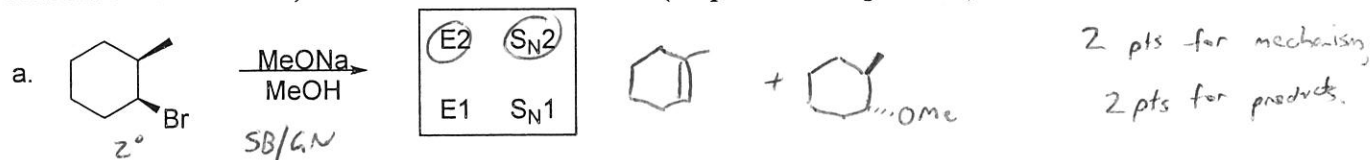
- d. Rank products A, B, and C from greatest quantity produced to least quantity produced. Explain why this is the case in under 20 words. (5 pts)

A > B > C, because this goes from most stable (most substituted) alkene to least stable.

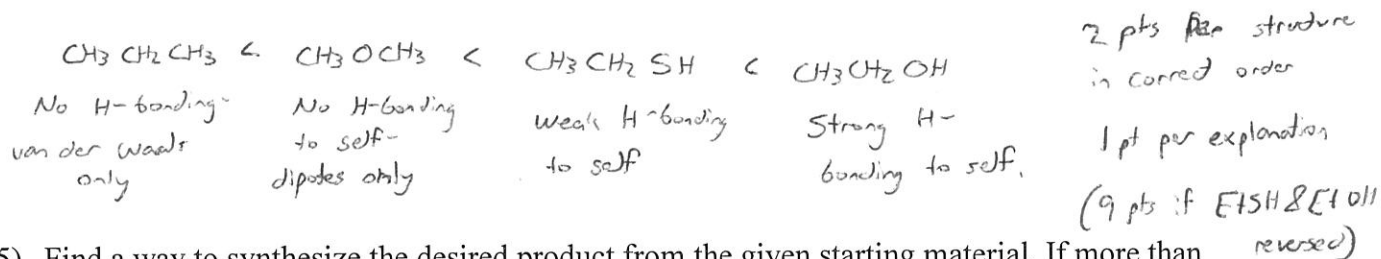
- 2) Each of these reactions can be done in a single step. On each arrow, show the reagents needed to accomplish each one. In each case, the target product should be the major product of the reaction. (12 pts – 3 pts each)



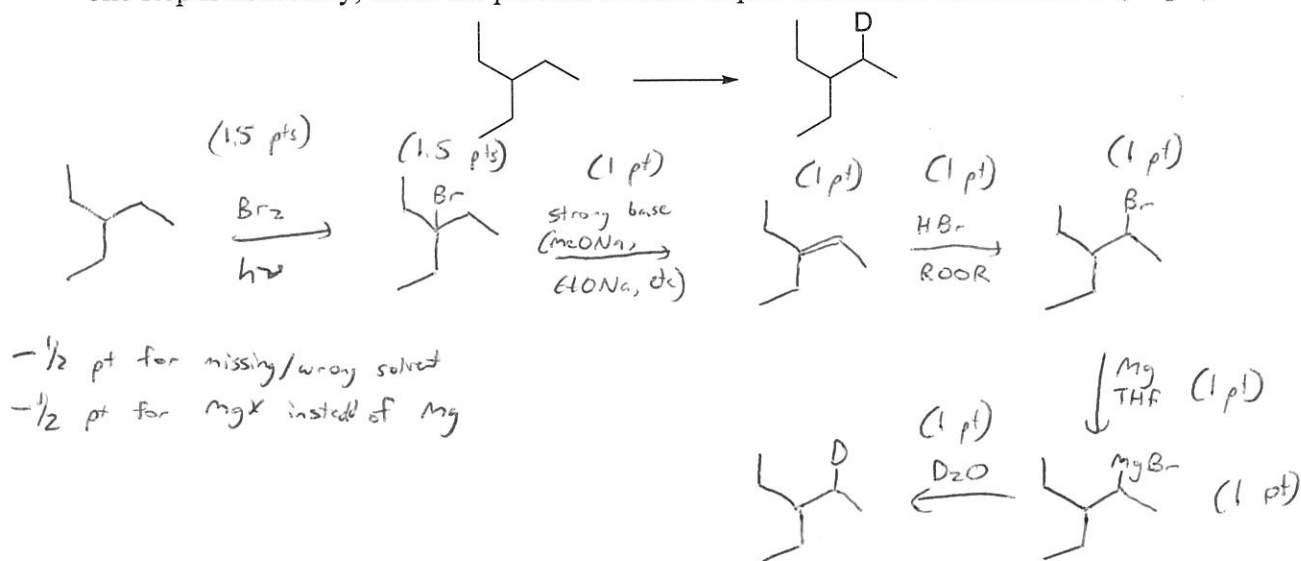
- 3) For each of the reactions shown below, **circle the mechanism(s)** you would expect to see, if any, and **draw the product(s)**. If a product has stereocenters, show its configuration using wedges and dashes. If two stereoisomers are formed, show both of them. If an elimination occurs, show only the major alkene product. If none of the mechanisms would take place in a reasonable time frame, write NR for No Reaction. (16 pts total - 4 pts each)



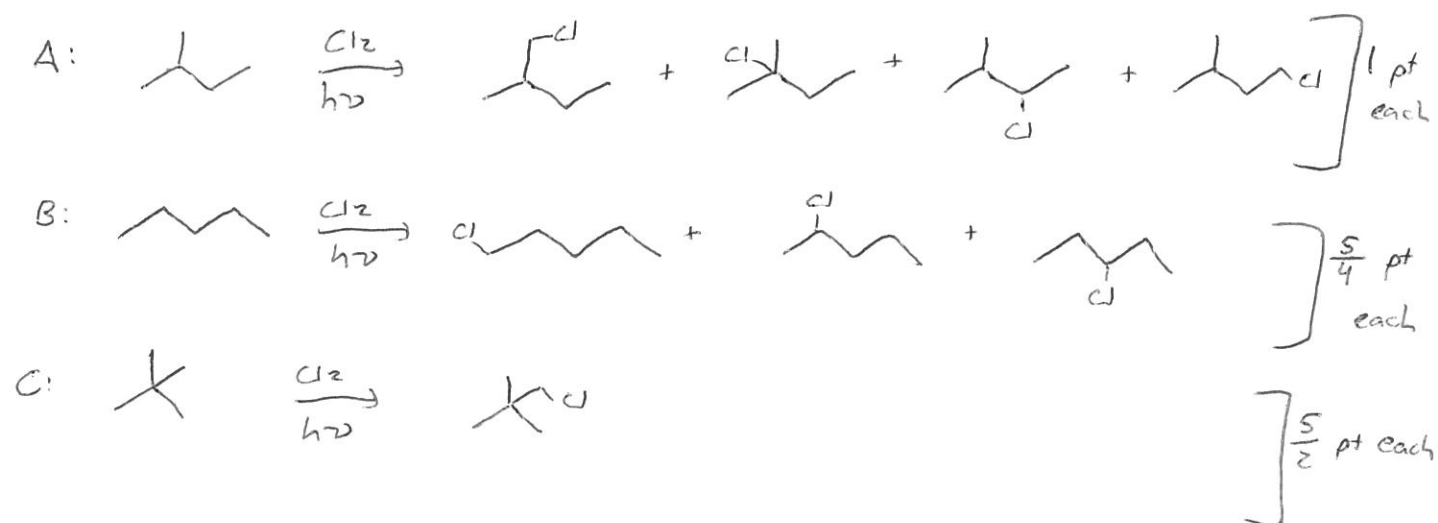
- 4) Arrange these compounds in order of increasing boiling point: $\text{CH}_3\text{CH}_2\text{OH}$, CH_3OCH_3 , $\text{CH}_3\text{CH}_2\text{CH}_3$, and $\text{CH}_3\text{CH}_2\text{SH}$. In under ten words per compound, explain what properties of each compound are responsible for raising its boiling point. (12 pts)



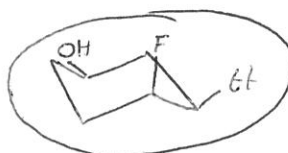
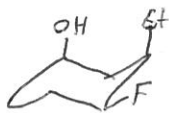
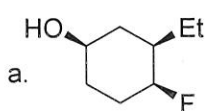
- 5) Find a way to synthesize the desired product from the given starting material. If more than one step is necessary, show the product of each step. Do not show mechanisms. (10 pts)



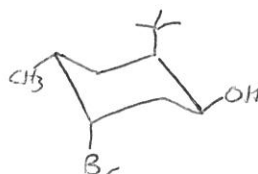
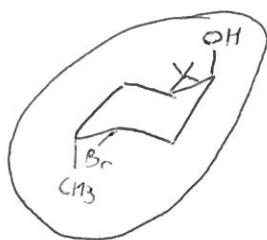
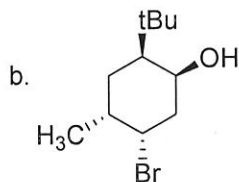
- 6) Three different constitutional isomers have the formula C_5H_{12} . When treated with chlorine and UV light, isomer A gives a mixture of four monochlorination products, isomer B gives a mixture of three monochlorination products, and isomer C gives a single monochlorination product. Based on this information, draw the structures of A, B, and C, and draw each of the monochlorination products that they form. (15 pts - 5 pts each)



- 7) For each of the following structures, show both chair conformations. (Make sure your bond angles clearly indicate whether each group is equatorial or axial.) Circle the more stable ring-form for each molecule. (15 pts total - 5 pts each)

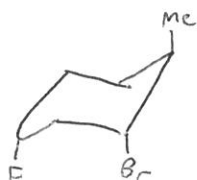
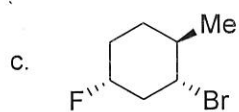


2 pts per structure,
1 pt per correct circle.



-1/2 pt per bond drawn at
bad angle

-1 for showing enantiomer of
actual molecule.

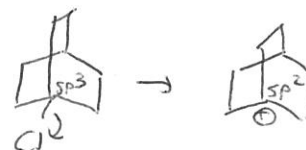


- 8) Extra credit! 1-chlorobicyclo[2.2.1]heptane, shown below, is virtually unreactive in the S_N1 reaction despite being tertiary. In fact, it has been estimated that it is 10^{13} times slower at S_N1 than *tert*-butyl chloride. In twenty words or less (but drawing any structures that are necessary), explain why this is the case. (Hint: what geometry does the intermediate structure have?) (5 pts extra credit)



During S_N1 , the carbocation is sp^2 :

The geometry at this carbon makes it difficult to get trigonal planar geometry, due to ring strain.



0 pts for "steric hindrance" or "accessibility to nucleophile"