Chemistry 3A - Spring 2000
Midterm 2

Professor Jean Fréchet

March 16, 2000

Your full signature

Print your full name
(Last name, First name, Middle)

Your SID

Please check the section number and name of your GSI/TA.

___161 Verdugo,Dawn
___171 Klopp,John
___181 Borths,Christopher
___191 Fujdala,Kyle
___111 Watkins,Gregory
___121 Blackwell,Bethany
___131 Fox,Daniel
___141 Werkema,Evan
___261 Peterka,Darcy
___271 Lee,Charles
___211 Tripp,Jennifer
___221 Padilla,Omayra
___361 Haman,Kristina
___371 Hecht,Stefan
___311 Saxon,Eliana
___321 Cook,Brian
___461 Purdy,Matthew
___471 Evans,John
___411 Holland,Andrew
___421 Duncan,Andrew
___431 Trimble,Alexander
___511 Marcaurelle,Lisa
X 521 Jen,Wendy
___531 Ling,Frank

If you are making up an I-grade, indicate the semester you took 3A_____ and the Professor_____.

This exam has **10** pages; **make sure that you have them all.** We will only grade answers that are in the designated spaces. Please do your scratch work on the backs of the exam pages. Write only **one** answer to each problem; multiple answers will receive **no** credit, even if one of them is correct.

Note: This examination runs for a total of 90 minutes. No questions will be answered by proctors after the exam begins. Please write legibly; ambiguous or messy answers will receive **no credit**.

A partial periodic table and data needed for calculations can be found on page **10** of the exam.

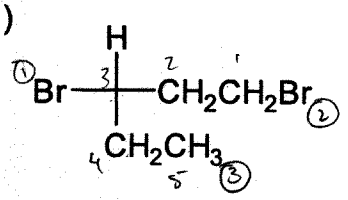
Do Not Write in this Box.

1.	9	(9)
2.	10	(12)
3.	9	(10)
4.	9	(15)
5.	5	(12)
6.	18	(17) 18
7.	7	(12)
8.	7	(12)
Total	74	(100)

1. (9 points)

Name or draw, as appropriate, the following molecules. Do not forget stereochemistry where appropriate.

(a)

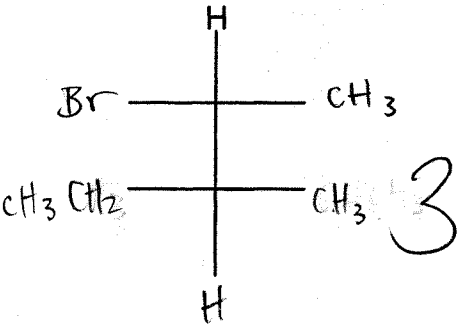


(IUPAC name)

(3R)- 1,3- dibromopentane 2

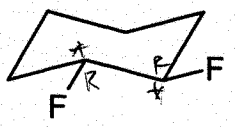
(b) (2S,3S)-2-bromo-3-methylpentane

(Fischer Projection)



3

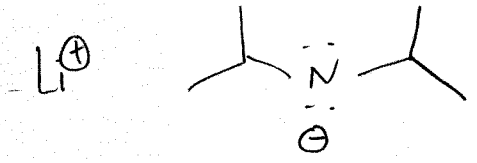
(c)



(IUPAC name)

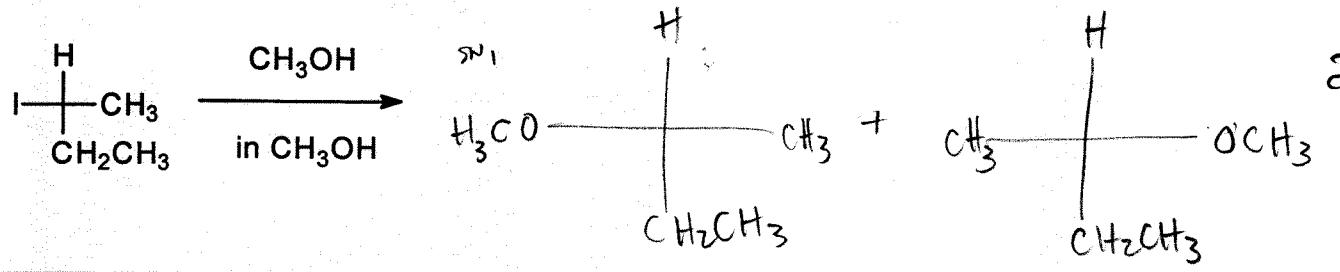
trans - 1,2 - difluorocyclohexane 2

(d) Lithium diisopropylamide



2

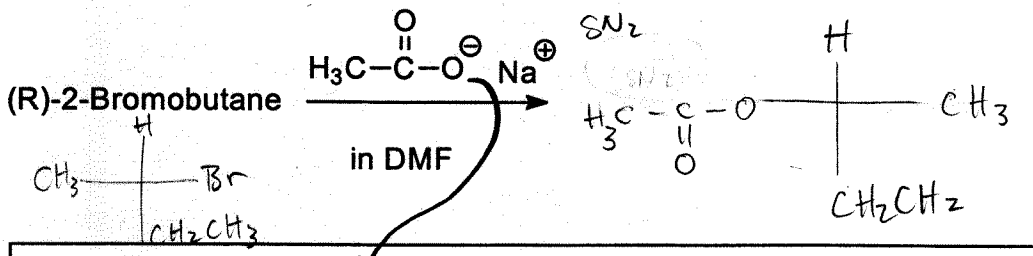
2. (12 Points). (a) Consider the two different substitution reactions shown below. Assume that **no** elimination side-reaction takes place. Draw a clear **Fischer projection** for each product(s) obtained in each of these reactions; also write an equation showing the **RATE law** for each reaction.



2

Rate = k [(S)- 2-iodobutane] ~~racemic mix so R & S are present~~ in equal amts

2

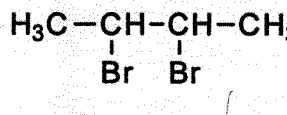


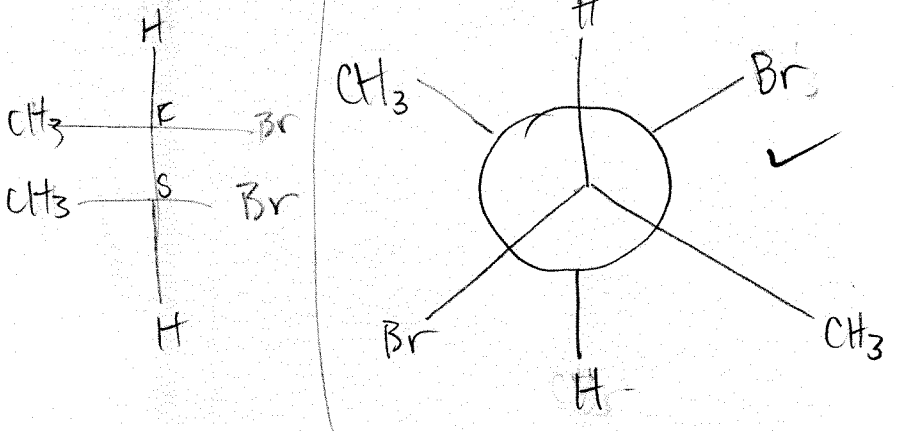
2

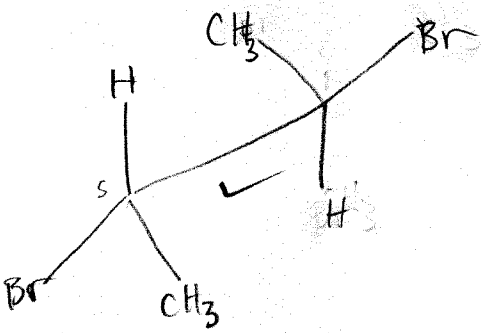
Rate = k [~~DMF~~] [(R)-2-bromobutane]

0

(b) Draw a Newman projection and a sawhorse projection for the most stable conformation of meso-2,3-dibromobutane







4

/10

3. (11 points) (a) A partly racemized mixture of enantiomers of limonene with an optical purity of 80% has an optical rotation of +92°. Given that (R)-limonene is known to have a positive optical rotation, calculate the percentage of (S)-limonene in the mixture and the optical rotation of pure (S)-limonene. Show the equation used and also the details of your calculation.

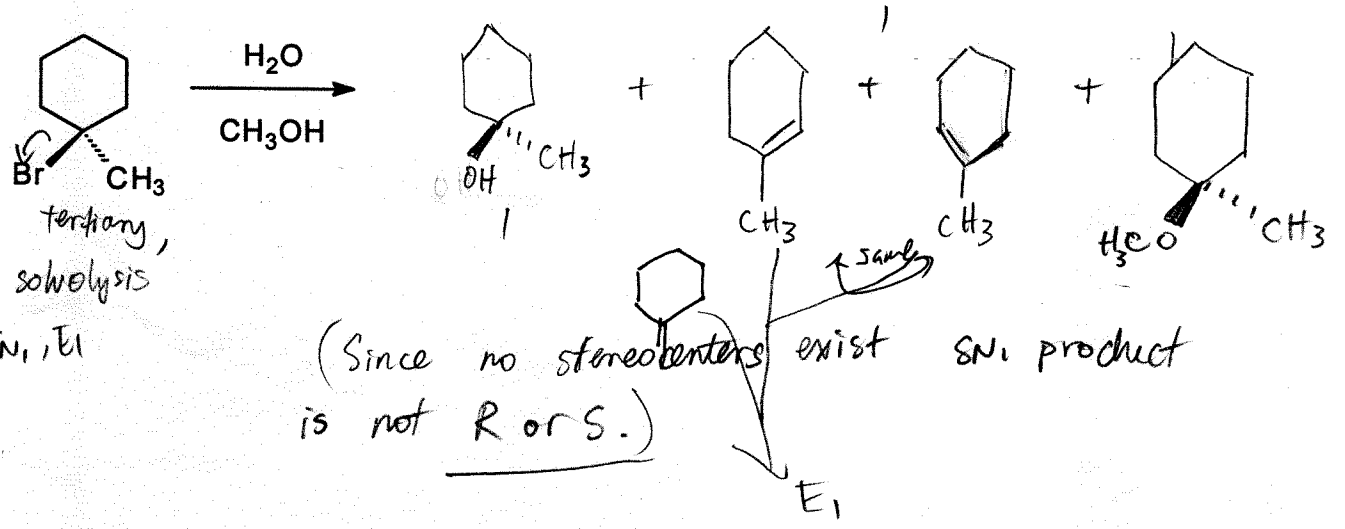
80% R
20% racemic
10% (S) 90% (R)

$(+92°) = [\alpha]_D (.80)$

$[\alpha]_D = +115°$ of (R)

Answers. % of (S) in mixture= 10% (2) Optical rotation of pure (S)-limonene: −115° (2)

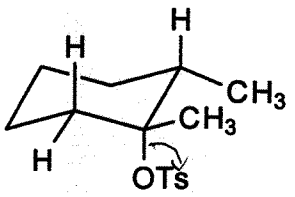
(b) Write clear structures for all of the products that may be formed when 1-bromo-1-methylcyclohexane reacts with a mixture of water and methanol. No mechanisms are needed.



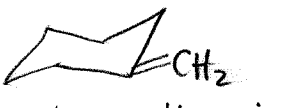
(Since no stereocenters exist SN1 product is not R or S.)

9

4. (15 points). (a) Complete the following reactions showing the structure of the MAJOR product. Show clear stereochemistry where appropriate. Write NR if there is no reaction.

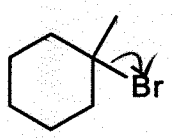


strong base
$EtO^{\ominus}\ Na^{\oplus}$
in EtOH
(tertiary halide) E_2
antiperiplanar

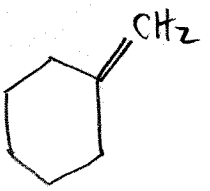


this isn't major

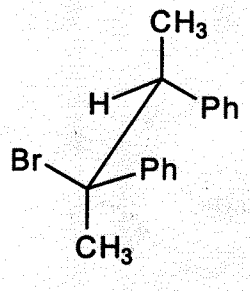
+ 1



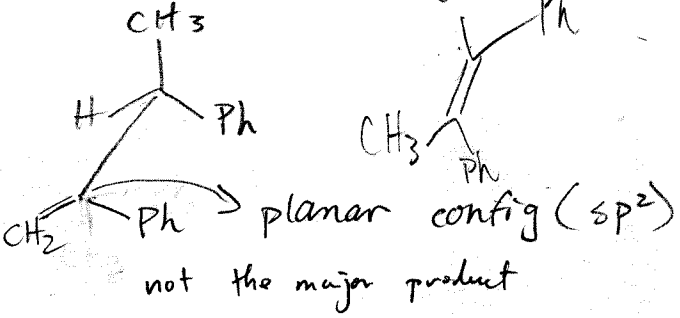
$K^{\oplus}\ t\text{-}BuO^{\ominus}$
in t-BuOH
E_2
tertiary



+ 3



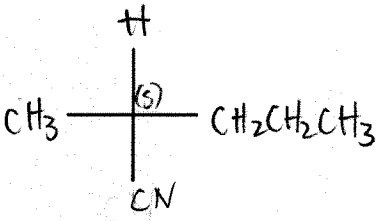
$Na^{\oplus}\ ^{\ominus}OH$
Δ
E_2
strong base



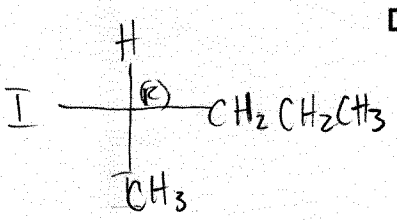
planar config (sp^2) + 1
not the major product

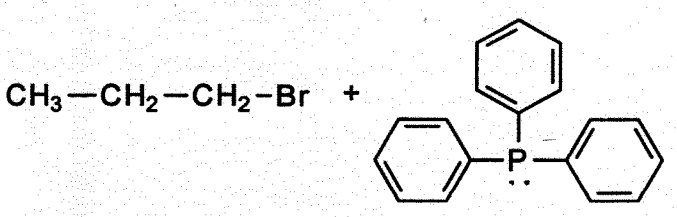
(R)-2-iodopentane

$Na^{\oplus}\ ^{\ominus}CN$
DMF
secondary
weak base
good Nu

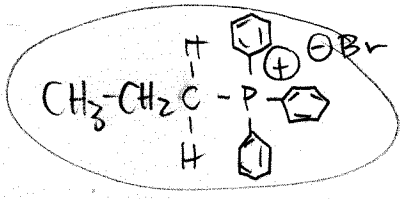


(show the product as a Fischer projection) + 3





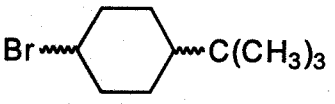
weak
hindered
~~base~~
primary
unbranched
S_N2

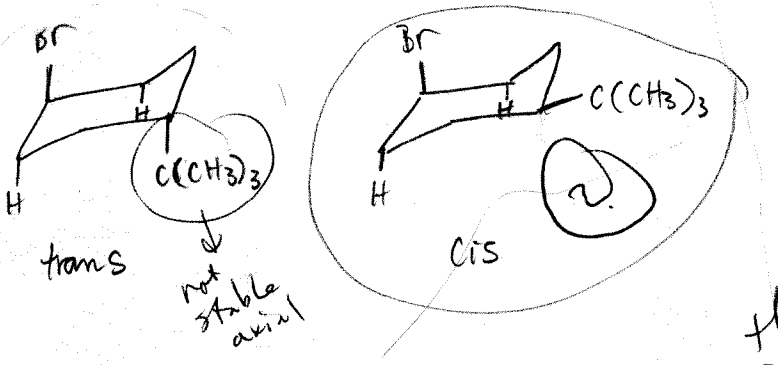


+ 1

9

5. (12 Points). (a) Which of the two stereoisomers of 1-bromo-4-t-butylcyclohexane will react **faster** in an E_2 Elimination reaction with $EtO^{\ominus}$ as the base? Draw clear chair structures of the two stereoisomers, **circle the most reactive** stereoisomer and explain briefly.

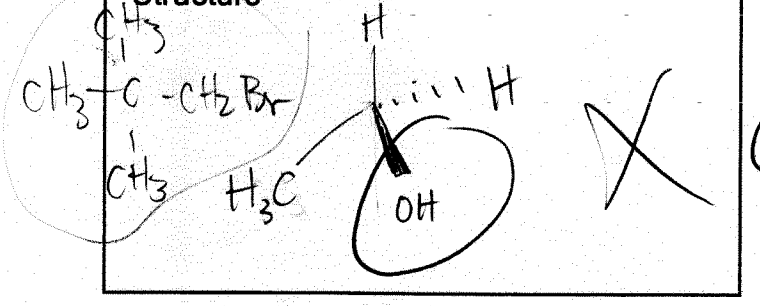




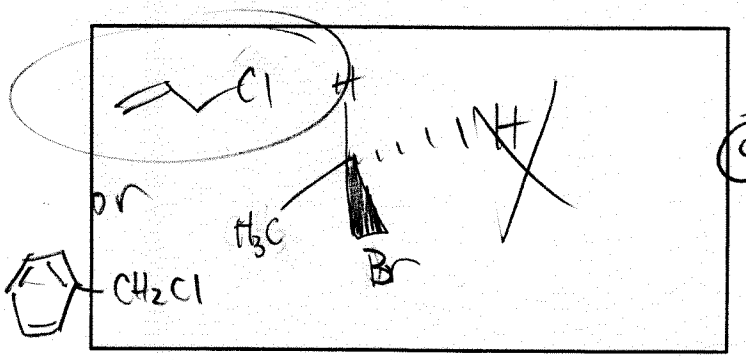
The cis stereoisomer will be more reactive (because the t-butyl substituent will not hinder the removal of antiperiplanar (1) H^+ from the carbons adjacent to the carbon bearing the Br.

the t-Bu group locks the conformation (steric)

(b) Write a clear structure for a primary halide that is essentially unreactive in an S_N2 reaction and give a brief explanation of your answer

Structure	Brief explanation
	OH is a poor leaving group Too much hindrance

(c) Write a clear structure for a primary halide that reacts easily in an S_N1 reaction and give a brief explanation of your answer

Structure	Brief explanation
	Br is ~~an~~ excellent leaving ~~group and the carbon bearing it has~~ allylic (benzylic halides form carbocations are stabilized by resonance

8 8 5

6. (17 points) (a) 20 milliliters of a solution containing 2.2 grams of a compound rotate the plane of polarized light +0.66° in a polarimeter with a 2 decimeter long sample tube. What is the specific rotation of the sample? Show equation and calculations.

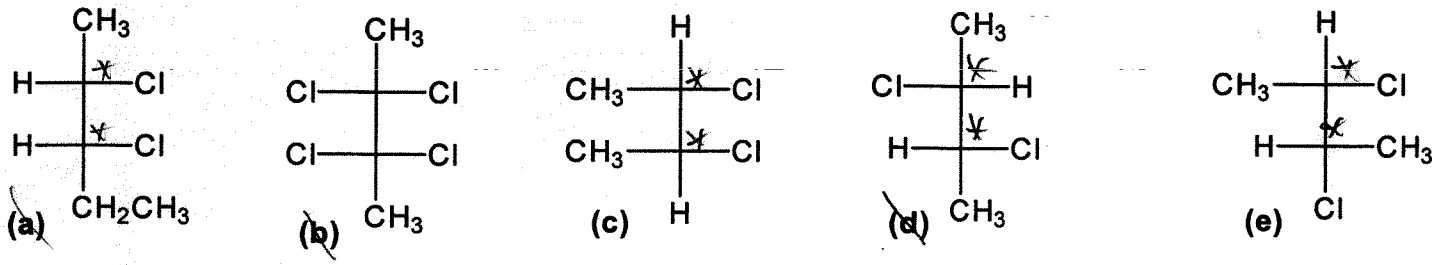
18

$$[\alpha]_D = \frac{\alpha}{l \cdot c} = \frac{+0.66^\circ}{(2\,dm)\left(\frac{2.2\,g}{20\,mL}\right)} = 3.0^\circ$$

3

Answer: 3.0°

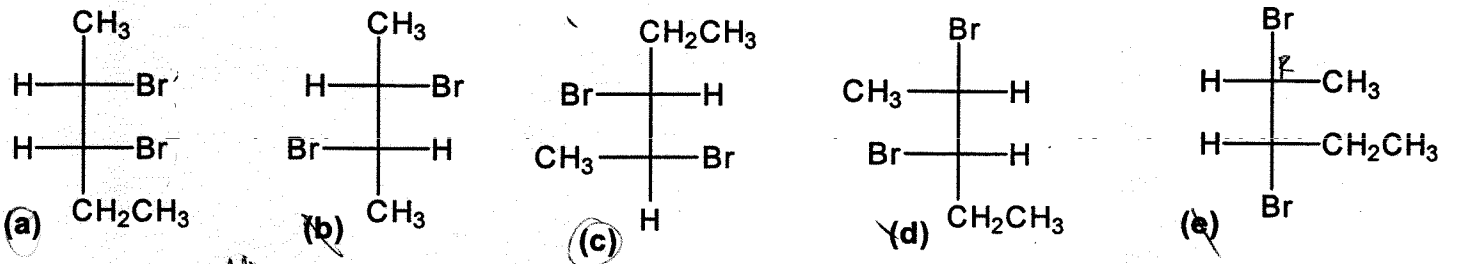
(b) Which of the following are meso compounds? Write the answer(s) in the box provided but do not guess as wrong answers will results in point deductions from correct answers.



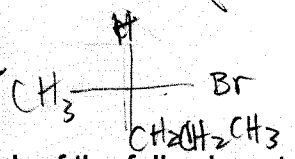
4

Answer(s): C, e

(c) When (S)-2-bromopentane is brominated, several 2,3-dibromopentanes are formed. Which of the following are formed? (Note: wrong answers will result in point deductions).



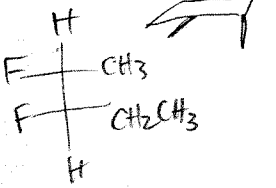
6



Answer(s): a, c, d,

(d) Which of the following statements are **FALSE**? (Note: wrong answers will result in point deductions)

(1) A compound with three asymmetric carbons may have up to nine stereoisomers. 8
(2) The most stable conformation of cis-1,2-dimethylcyclohexane has both methyls equatorial
(3) Meso compounds do not rotate polarized light T
(4) Diastereomers always have the same boiling points
(5) 2,3-difluoropentane has a stereoisomer that is a meso compound.
(6) R and S enantiomers always have the same specific rotation
(7) S_N2 reactions are second order reactions T
(8) S_N1 reactions involve carbocationic intermediates T

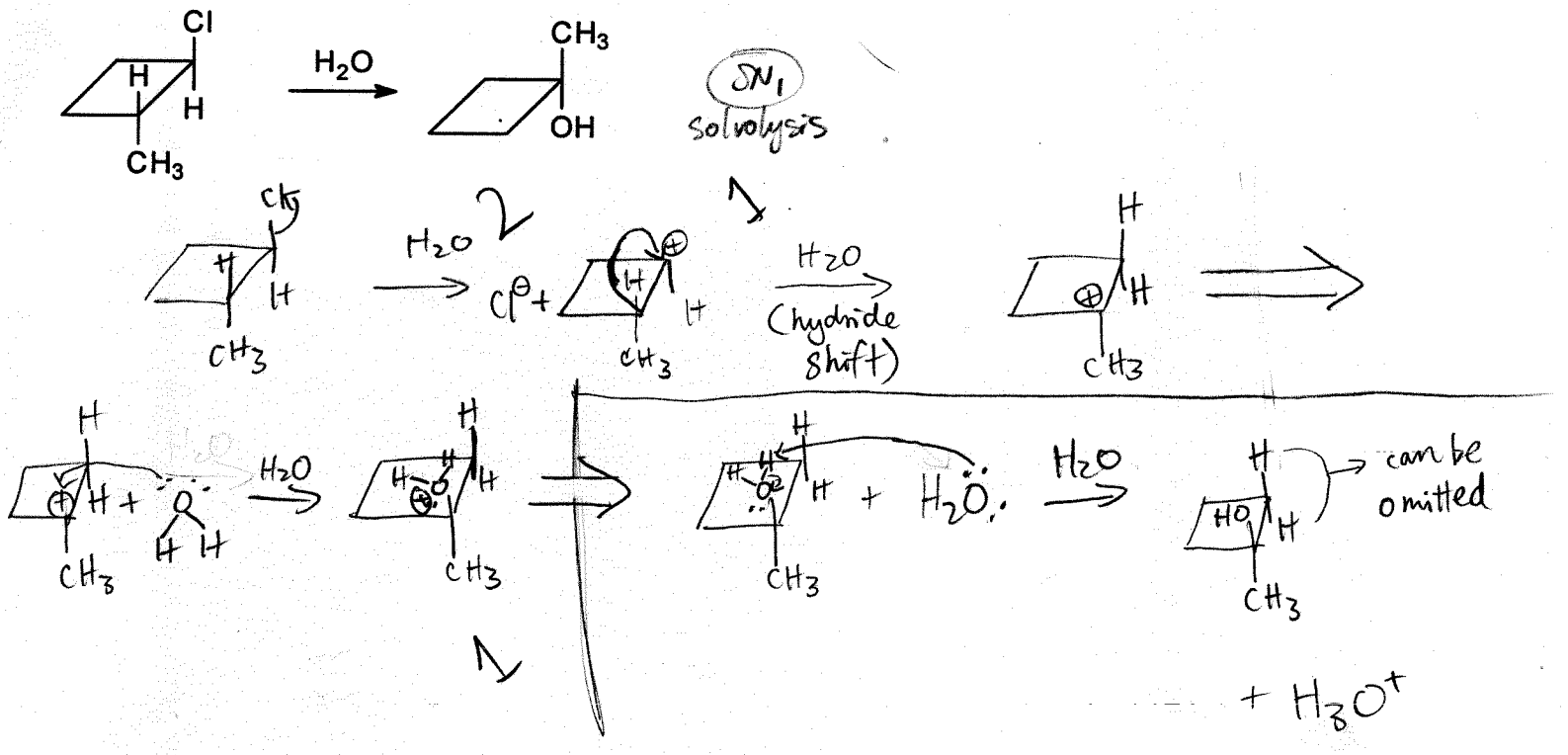


5

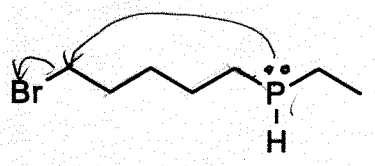
Answer(s): 1, 2, 4, 5, 6,

18

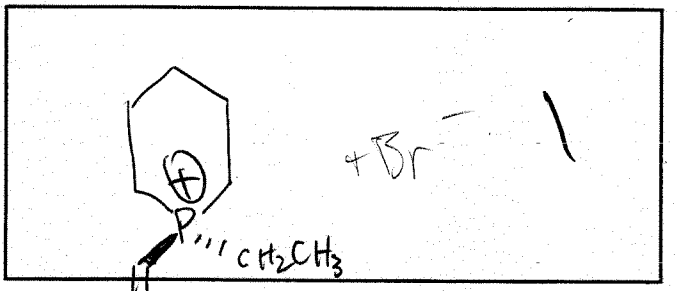
7. (12 points). (a) Write a step-by step mechanism (include arrows) for the reaction below:



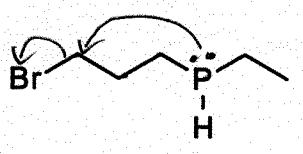
(b) The compounds shown below both react spontaneously at room temperature. Which of the two reactions is fastest and why? Show the structures of the products and explain your answer.

(i) 

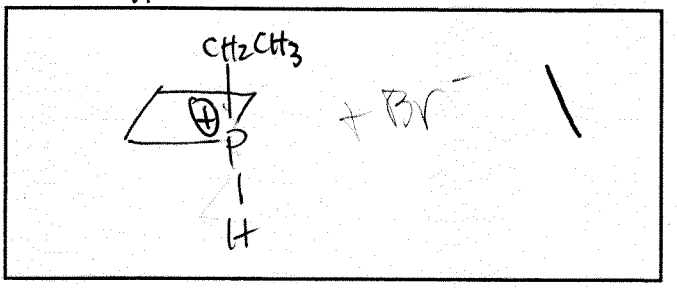
DMF



SN2

(ii) 

DMF

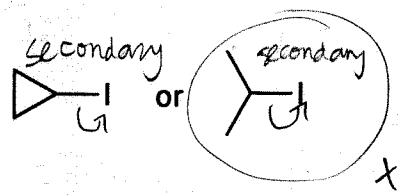


Fastest reaction is: i Explanation: The product formed is a 6-carbon ring and is more stable than the 4-carbon ring formed in ii. lower Ea

6-ring has less strain

7

8. (12 Points) (a) Which of the following alkyl iodides will react faster in a reaction with $Na^{\oplus}{}^{\ominus}CN$ in DMF?



Circle your answer and provide a brief but clear explanation for the difference in reactivity.

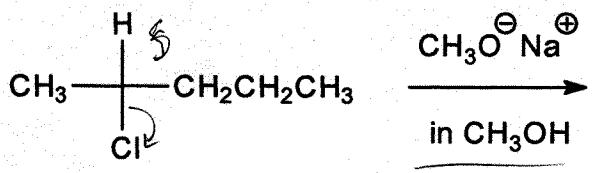
+1 S_N2

Explanation: The pathway is S_N2 (aprotic polar solvent and good nucleophile, weak base) so the less hindered the central carbon, the faster the reaction, ring strain (120° transition state is hard to achieve w/ #1)

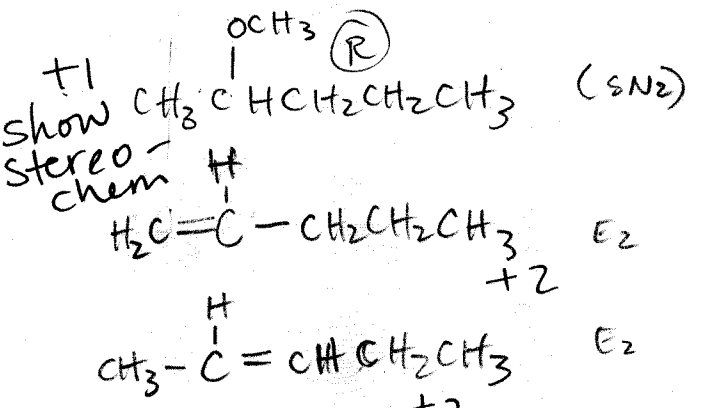
+1

oops, SN1 & ↗

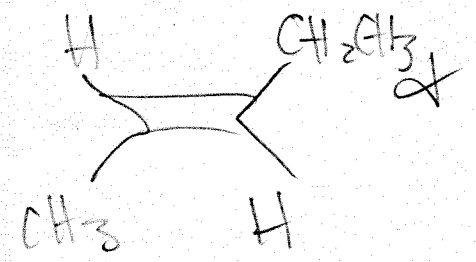
(b) Show **ALL** the products obtained in the following reaction (no mechanism needed):

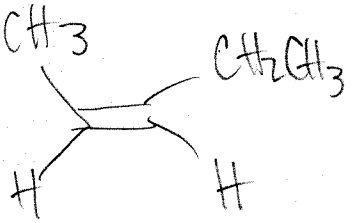


+1 show stereochem



show cis/trans





7

Note: **There are no questions to be answered on this page**, it only contains data that may be of use in solving the questions contained in this exam. Not all of the data given is needed.

Value of gas constant: R = 2.0 cal deg^{-1} mol^{-1}

Value of e (base for natural logarithms) e = 2.718

Value of absolute zero (kelvin) = -273°C

Partial periodic table of the elements

GROUP	I A	II A	III B	IV B	V B	VI B	VII B	0
VALENCES	+1	+2	+3	−4 +4	−3 +5	−2 +6	−1 +7	0
PERIOD 1	1 H 1.008							2 He 4.003
2	3 Li 6.941	4 Be 9.012	5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
3	11 Na 22.99	12 Mg 24.31	13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
4	19 K 39.10	20 Ca 40.08	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
5	37 Rb 85.47	38 Sr 87.62	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3