Chemistry 3A - Fall 1998
Midterm Exam 3

Professor Jean Fréchet

November 12, 1998

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.

___111 Turculet,Laura
___121 Klei,Steven
___131 Krumper,Jennifer
___141 Downey,Karen
___211 Eng,Christina
___221 Shiau,Timothy
___311 Kita,Ryoko
___321 Davis,Anna
___331 Yeh,Robert
___341 Mork,Benjamin
___361 Fischer,Fabian
___371 Bennett,Miriam
___381 Fujdala,Kyle
___411 Hodges,Alan
___421 Ahrendt,Kateri
___431 Borths,Christopher
___511 Saxon,Eliana
___521 Wiener,John
___531 de Graffenried,Christopher
___541 Dosa,Peter

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 80 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.

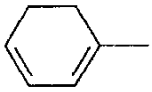
1._____(8)
2._____(10)
3._____(9)
4._____(10)
5._____(10)
6._____(9)
7._____(8)
8._____(11)

Total_____(75)

1. (8 points)

1. Name or draw, as appropriate, the following molecules according to IUPAC rules. Do not forget stereochemistry where appropriate.

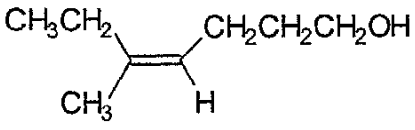
a.



b. (2R,3R)-2,3-butanediol

Fisher Projection only

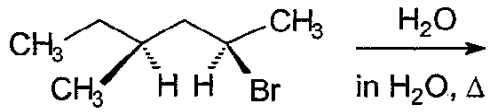
c.



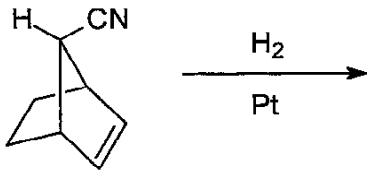
d. 1-chlorobicyclo-[2.2.1]heptane

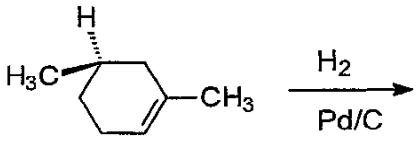
2. (10 points)

(a) Write a clear **stereochemical structure** for each of the products obtained in the following reaction. (No mechanism is needed)



(b) show the product(s) obtained in each of the following reactions:





3. (9 points) Heating CH_2=CH-CH_3 with HBr and a peroxide RO-OR affords 1-bromopropane.
(a) Write a detailed mechanism (with **all necessary curved arrows**) showing **the** two initiation steps of this reaction and explain clearly why it is necessary to heat the reaction mixture.

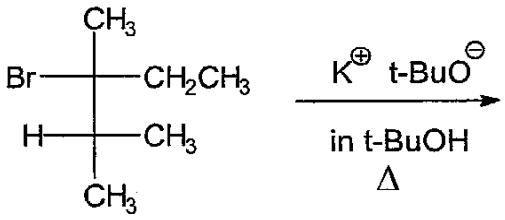
(b) Write the propagation steps and calculate the value of ΔH^0 for the overall reaction shown below:

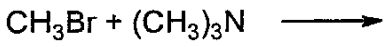
$$CH_2{=}CH{-}CH_3 + HBr \longrightarrow BrCH_2{-}CH_2{-}CH_3$$

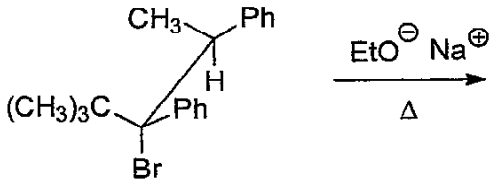
Your answer must show clearly the details of your calculation of ΔH^0 (NO mechanism needed).

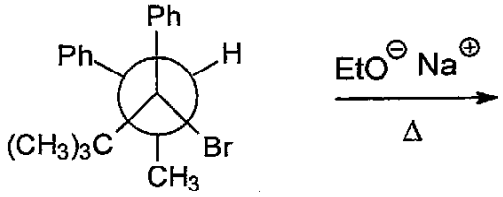
Answer: ΔH^0 =

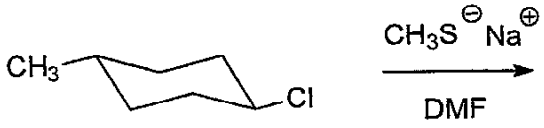
4. (10 points). Show the structure of the **major** product obtained in each of the following reactions. Your answers must show **clear stereochemistry** where applicable. If no reaction occurs, write NR. Do not show any mechanisms.





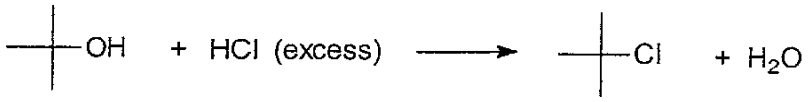




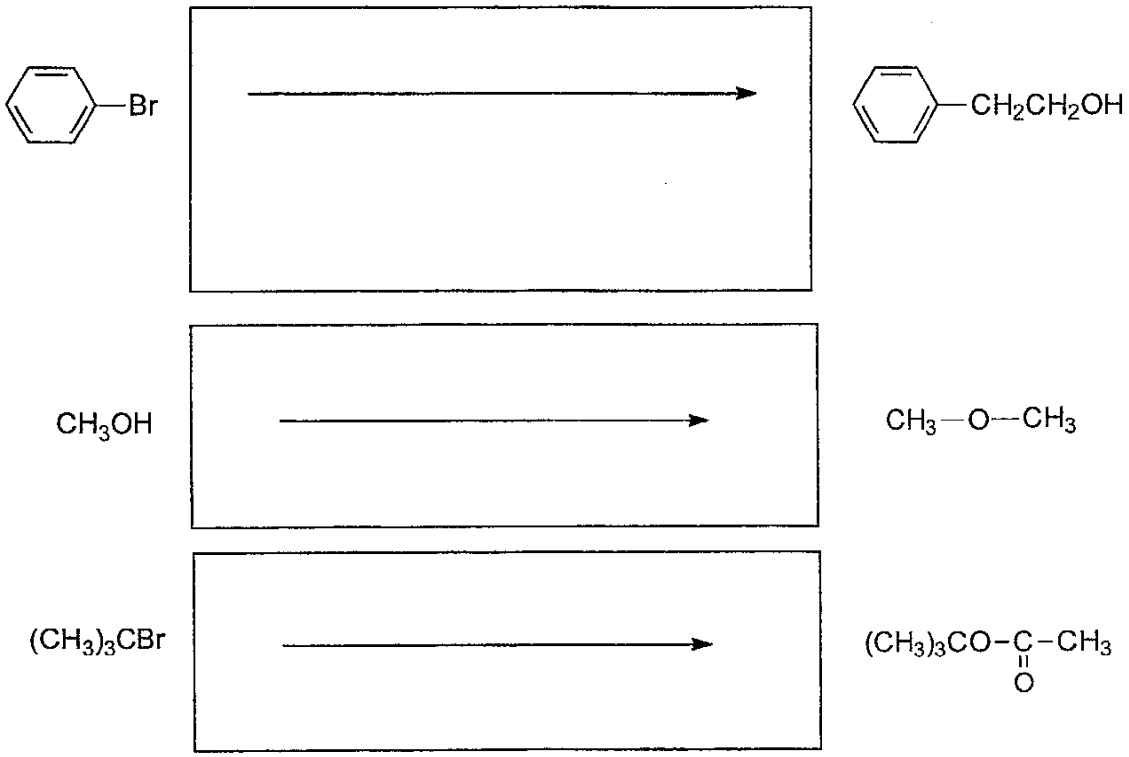


5. (10 points)

(a) Show a step-by-step mechanism (**with all curved arrows**) for the reaction below:

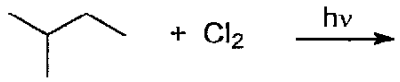


(b) Complete the reactions below showing all the missing **reagents** (and key **solvents** if appropriate). In all cases the choice of reagent must be such that the product shown is the major product of the reaction.

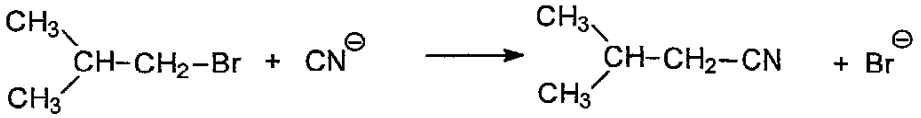


6. (9 points)

(a) The relative reactivity of primary, secondary and tertiary hydrogens towards chlorination is 1:4:5. Show a **clear structure** for **each** of the products that may be obtained by monochlorination of 2-methylbutane, and **circle** the product obtained in highest yield in this monochlorination reaction. (Note: do not write any additional or duplicate structure, no detailed calculation is needed)



(b) Write the rate law for the following reaction:

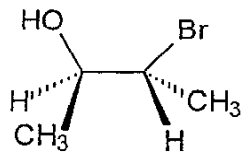


ANSWER:

(c) In the above reaction has a relative rate of 1, what would be the relative rate of reaction if the concentration of **both** the alkyl bromide and the CN^- were tripled?

ANSWER: Relative rate =

7. (8 points) (a) Treatment of the bromohydrin (shown below) with sodium hydroxide affords a bromine-free product with the formula C_4H_8O. Show a clear stereochemical representation of this product and write a step-by-step mechanism (with curved arrows) to explain its formation. *(Hint: to be complete your answer must show a clear conformation of the key reactive intermediate)*



NaOH
in DMF

C_4H_8Br

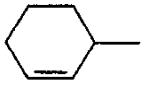
(b) What type of reaction is involved in the above process? (write the letter of the appropriate answer in the box)

ANSWER:

(A) Hydrogenation (B) Radical reaction (C) S_N1 reaction

(D) S_N2 reaction (E) E_1 reaction (F) E_2 reaction (G) Rearrangement

8. (11 points) No mechanisms are needed in this question

(a) Propose a step by step synthesis of  starting from  and CH_3Br

You may use common reagents as needed

(b) Propose a step by step synthesis of $H_3C-\underset{\displaystyle D}{\underset{|}{CH}}-CH_3$ from $H_2C=CH-CH_3$

You may use common reagents as needed

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

Bond dissociation energies (in Kcal $mole^{-1}$) for the covalent bonds shown:

$CH_2{=}CHCH_3$ (Π bond only: 66)

$CH_2{=}CHCH_3$ ($\sigma + \Pi$ bonds: 151)

$CH_3CH_2CH_2{-}Br$ (69)

$CH_3CH_2CH_2{-}I$ (54)

$CH_3{-}Br$ (70)

$CH_3{-}H$ (104)

RO—OR (35)

Br—Br (46)

I—I (36)

$CH_3CH_2CH_2{-}H$ (98)

CH_3CHCH_3 (95)
|
H

H—Br (87)

H—I (71)

$CH_3{-}CH_3$ (88)

$CH_3CH_2{-}CH_3$ (85)

RO—H (103)

Partial periodic table of the elements

IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII			IB	IIB	IIIA	IVA	VA	VIA	VIIA	O
1 H 1.00794																	2 He 4.00260
3 Li 6.941	4 Be 9.01218											5 B 10.811	6 C 12.011	7 N 14.0067	8 O 15.9994	9 F 18.9984	10 Ne 20.1797
11 Na 22.9898	12 Mg 24.3050											13 Al 26.9815	14 Si 28.0855	15 P 30.9738	16 S 32.066	17 Cl 35.4527	18 Ar 39.948
19 K 39.0983	20 Ca 40.078	21 Sc 44.9559	22 Ti 47.88	23 V 50.9415	24 Cr 51.9961	25 Mn 54.9381	26 Fe 55.847	27 Co 58.9332	28 Ni 58.69	29 Cu 63.546	30 Zn 65.39	31 Ga 69.723	32 Ge 72.61	33 As 74.9216	34 Se 78.96	35 Br 79.904	36 Kr 83.80
37 Rb 85.4678	38 Sr 87.62	39 Y 88.9059	40 Zr 91.224	41 Nb 92.9064	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.906	46 Pd 106.42	47 Ag 107.868	48 Cd 112.411	49 In 114.82	50 Sn 118.710	51 Sb 121.75	52 Te 127.60	53 I 126.904	54 Xe 131.29
55 Cs 132.905	56 Ba 137.327	57 La • 138.906	72 Hf 178.49	73 Ta 180.948	74 W 183.85	75 Re 186.207	76 Os 190.2	77 Ir 192.22	78 Pt 195.08	79 Au 196.967	80 Hg 200.59	81 Tl 204.383	82 Pb 207.2	83 Bi 208.980	84 Po (209)	85 At (210)	86 Rn (222)