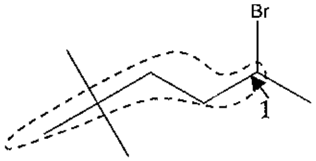
Exam II: Organic Chemistry I Alfred State College ______/100 pts Monday 3 Nov
Your Name: ______________________________ (1 pt)

I. **Names and Structures** (2 pts each/14 points total)

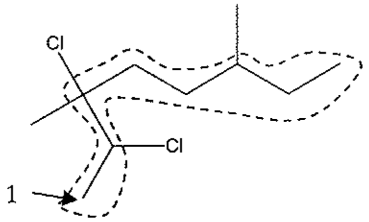
Provide the correct name or structure below. Use IUPAC rules unless otherwise indicated.

a)



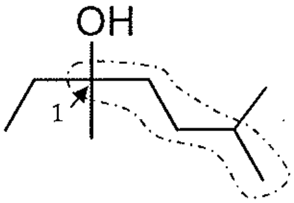
_1,4,4-trimethylpentyl bromide_____________
functional group form

b)



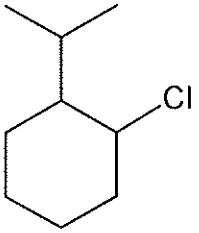
_2,3-dichloro-3,6-dimethyloctane_______
IUPAC

c)



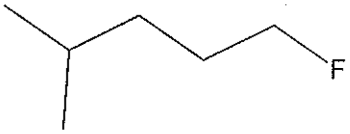
1-ethyl-1,4-dimethylpentyl alcohol_______
functional group form

d)



__________ **1-chloro-2-(1-methylethyl)cyclohexane**
IUPAC

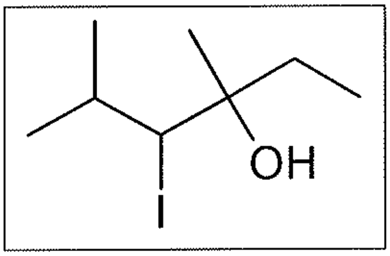
e)



isohexyl fluoride

____
common name

f)



1-ethyl-2-iodo-1,3-dimethylbutyl alcohol

n-pentyl bromide______

Common name

____/15 (includes name pt)

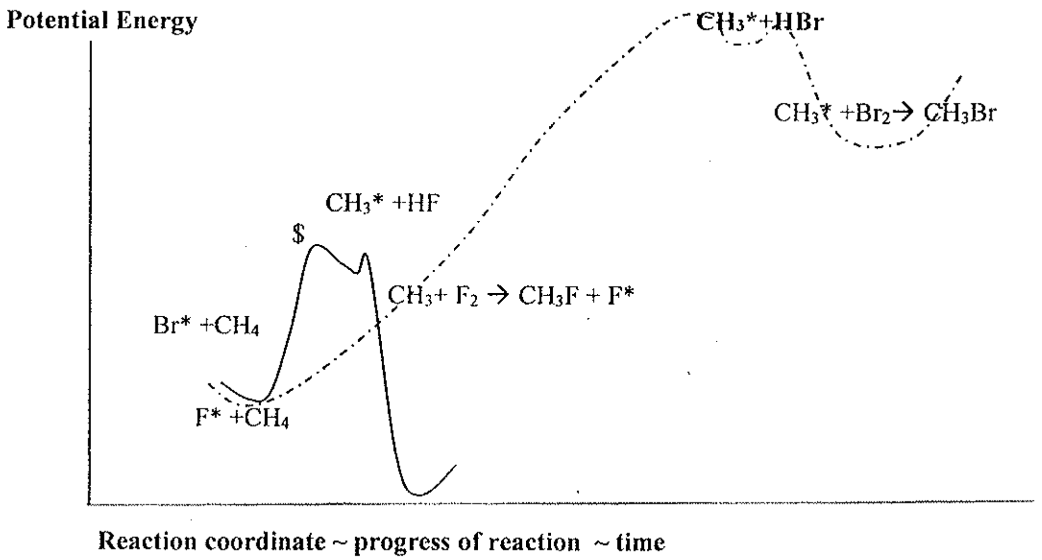
II. Higher Alkanes and Potential Energy Diagrams 11 pts

a) Name the two major facts about the free radical halogenation of higher alkanes that are not in the original list of 5 facts connected to the free radical halogenation of methane: (2 pts)

1) **rate follows 3° >2° >1° >0**

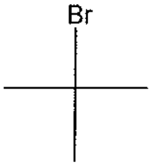
2) **I > Br> Cl > F for selectivity**

b)Draw the energy diagrams associated with the free radical halogenation of methane with F and Br below starting from the chain propagation step (X* + CH_4) : (4 pts)

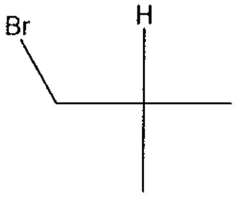


c) Given the relative reactivities below, estimate the % yield for A and B. Show work. 6 pts

C degree	R
1°	1
3°	100



A



B

	A	B
% yield	91.75	8.25

For 1° : #1° H* 1 = 9*1 =9
Fro 3° #3°H *100 =1*100 =100
sum 109

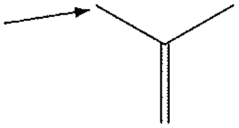
%yield 1° = 100(9/109)=8.25
% yield 3° =100(100/109)=91.75

____/12

II. Reactions to and from Alkyl Halides: Basic Facts and Vocabulary (16 pts)

1) For both S_N1 and S_N2 substitution of halogens on ROH, what is the common initial intermediate?
   ROH_2^+ protonated alcohol

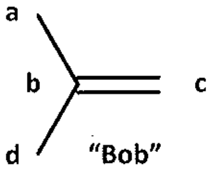
2) What name/term is used to describe the position shown here
   allylic
   ____



3) When addition of HBr across a double bond adds Br to the side containing the smaller groups=> anti-Markovnikoff______addition.

4) What is the order of reactivity for F^-, Cl^-, Br^-, I^- when substituting the OH on 1° alcohols ?
   ___I_____> ____Br________> _____Cl_____>_____F______

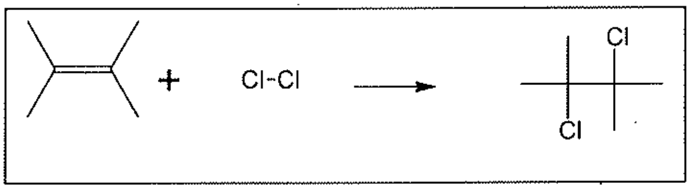
5) Where does OH go during haloydrin addition on Bob?
   a [✓ b] c d
   circle choice(s) above



6) Whose (variously spelled Russian) rule decides which is the most likely alkene formed from alkyl halides ? ___Saitzev rule_____(Zaitsev)__________

7) In the modern, solution phase reaction of alcohols to alkyl chlorides using pyridine, the common chloride source is the compound: _____$SOCl_2$____________

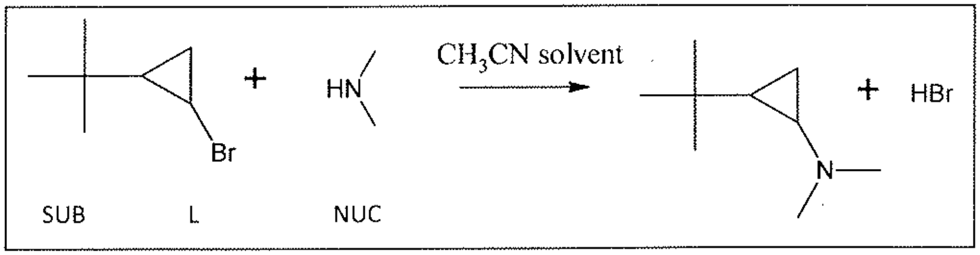
8) What solvent is commonly employed in the reaction shown below: __CCl_4__________



9) The reaction of KOH with 1-bromobutane to form an alkene is what class of reaction ?
   _________elimination______________________

10) What class of reactions leads to bigger alkanes and alcohols?_organometallic reagent preps_____

11) In the reaction below, clearly identify the substrate (Sub), nucleophile (Nuc) and leaving group (L): (3 pts)



12) Route to larger alkanes ______**Corey-House synthesis**_______________________

13) Route to larger alcohols:______Grignard synthesis_______________________

___/15

III. Mechanisms: Just the Facts (13 pts total)

In each pair, circle the outcome associated with S_N2 halogenation of alcohols (7 pts)

a)	[✓ product is inverted vs initial alcohol]	products are racemized
b)	rate increases in polar, protic solvent	[✓ rate increases in weakly-polar,non-protic solvent]
c)	[✓ rate increases with Br^- concentration]	rate indifferent to Br^- concentration
d)	[✓ rate increases with H+ concentration]	rate indifferent to H+ concentration
e)	unimolecular	[✓ bimolecular]
f)	[✓ requires reflux]	reflux unncesssary
g)	activated complex is 3-coordinated	[✓ activated complex is 5-coordinated]
h)	rearrangements occur	[✓ rearrangements don't occur]

In each pair, circle the outcome associated with S_N1 halogenation of alcohols (6 pts)

a)	both alcohol and halide affect rate	[✓ only alcohol affects rate]
b)	rate limiting step involves 5-coordinate complex	[✓ rate limiting step involves 3-coordinate intermediate]
c)	rate of reaction increases with non-protic polar solvents	[✓ rate of reaction increases with polar protic solvents]
d)	works only on 1° alcohols	[✓ works on 2° and 3° alcohols]
e)	rate varies sharply with attacking halogen	[✓ rate is indifferent to halogen]
f)	[✓ rearrangements occur]	rearrangements don't occur

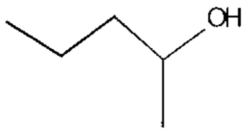
IV. Mechanistic Sooth-Saying (1 pt each/9 pts total)

<u>On speed (1 pt each/4 pts total)</u>

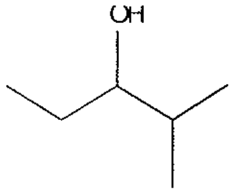
Which ~~will react faste~~r assuming HBr/ aqueous w/reflux is applied in each case ?

a) [✓ t-butanol] or sec-butanol **or ~ same**

b)

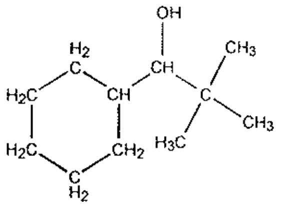


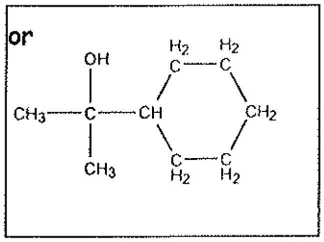
or



[✓ or ~same]

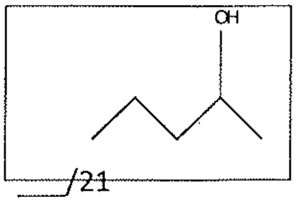
c)



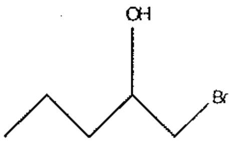


or ~same

d)



or



or ~same

Br destabilizes Carbocation

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Matchmaking (1 pt ea/5 pts total)

Match the mechanism to the acronym

Match from list

a) Mechanism for conversion of ethyl bromide to an ethene __SN2_

b) Mechanism for conversion of CH_3Br to CH_3NH_2: _SN2__

c) Mechanism for bromination of an alkane: __RAD_____

d) Mechanism for bromination of a 3° alcohol: __SN1_____

e) Mechanism involving formation of a racemic mixture __Sn1_

acronym

$S_n 1$

$S_n 2$

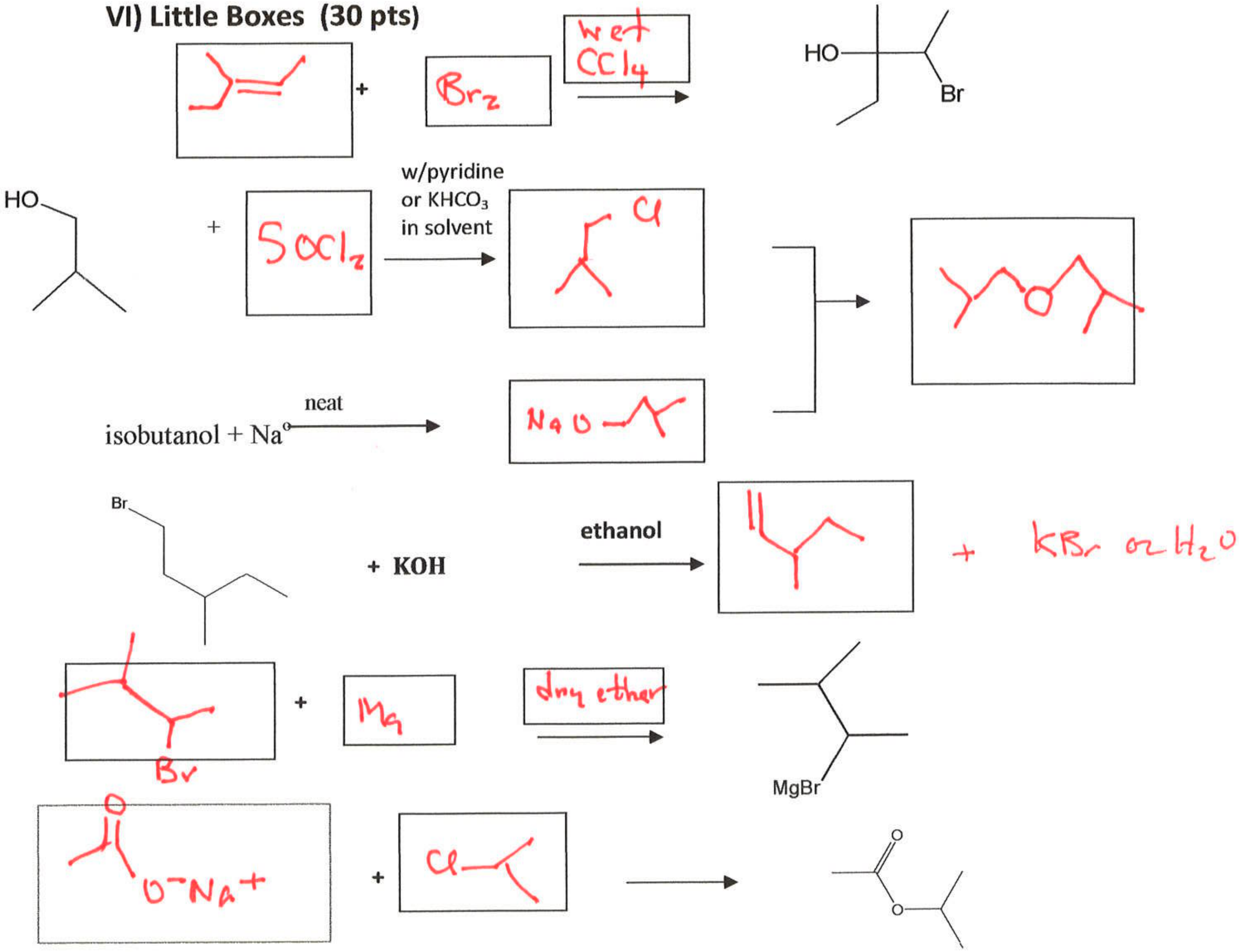
E2 (elimination)

RAD(free radical)

V. Random True/False (1 pt each/4 pts total)

1) racemization = scrambling of molecular handedness	T	F
2) The reaction of RMgX with H_2O is an oxidation	T	F
3) Mercaptans are the same as thiols	T	F
4) Halides are easier to substitute than –OH	T	F
5) Good nucleophiles are are soft, pudgy, \`easy' and fat with electrons	T	F

VI) Little Boxes (30 pts)



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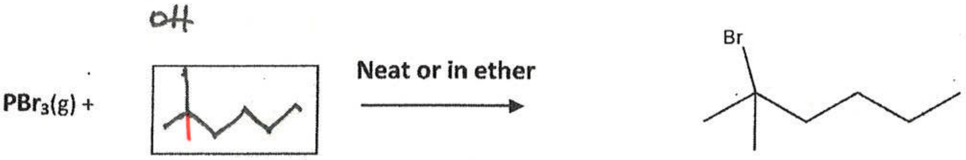
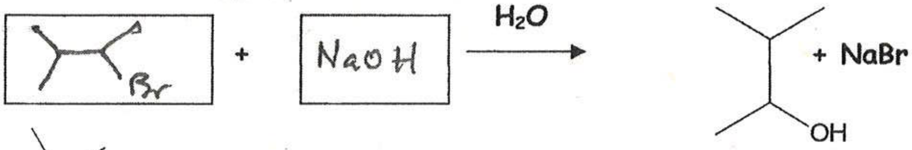
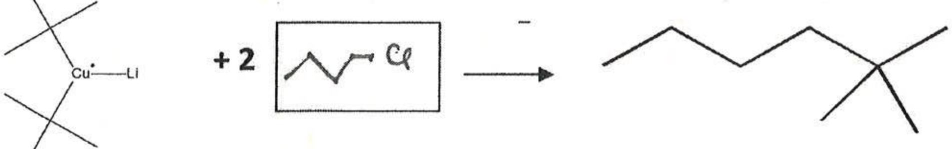
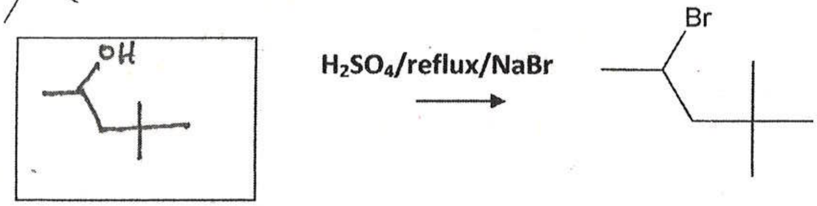
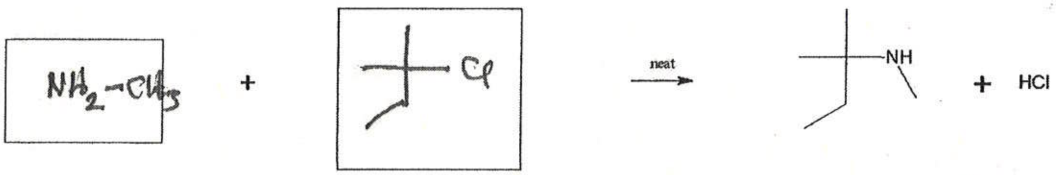
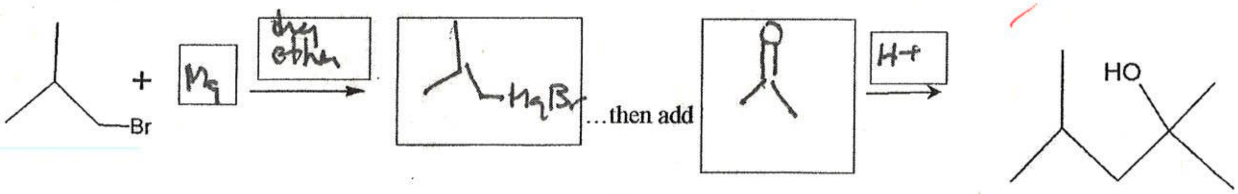

OH
PBr₃(g) +
Neat or in ether
Br

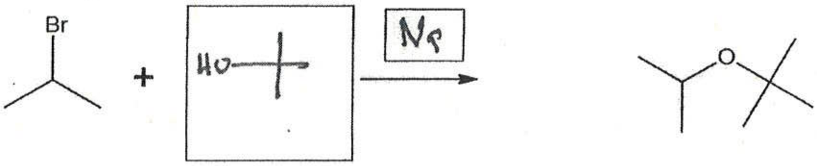

Br
+
NaOH
H₂O
+ NaBr
OH

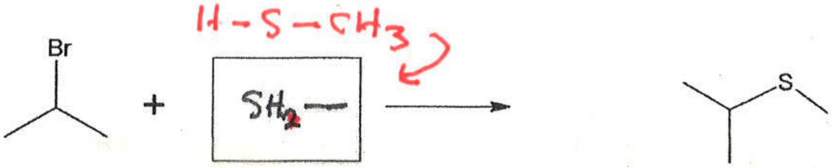

Cu
Li
+ 2
Cl

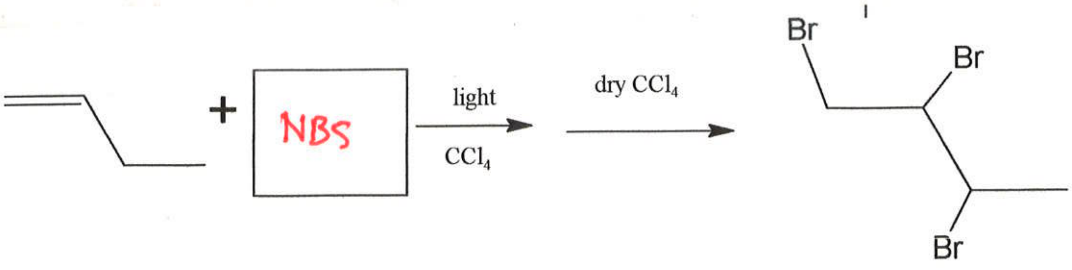

OH
H₂SO₄/reflux/NaBr
Br


NH₂–CH₃
+
Cl
neat
NH
+ HCl


Br
+
Mg
dry ether
MgBr
…then add
O
H+
HO


Br
+
HO
Na
O


H–S–CH₃
Br
+
SH₂
S


+
NBS
light
CCl₄
dry CCl₄
Br
Br
Br

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