Exam II: Organic Chemistry I Alfred State College \_\_\_\_\_\_/100 pts Monday 3 Nov

Your Name: \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ (1 pt)

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

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

a) b)





 1

 1

**\_\_1,4,4-trimethylpentyl bromide\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ \_2,3-dichloro-3,6-dimethyloctane\_\_\_\_\_\_\_\_\_**

functional group form IUPAC





c) d)

 1

**1-ethyl-1,4-dimethylpentyl alcohol\_\_\_\_\_\_\_\_\_ 1-chloro-2-(1-methylethyl)cyclohexane**

functional group form IUPAC





f)

e)

**isohexyl fluoride**

common name 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 3o >2o >1o >0**\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

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

2) \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

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\* + CH4) : (4 pts)

**Potential Energy CH3\*+HBr**

 CH3\* +Br2🡪 CH3Br

 CH3\* +HF

 $

 CH3+ F2 🡪 CH3F + F\*

 Br\* +CH4

 F\* +CH4

 **Reaction coordinate ~ progress of reaction ~ time**

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



**C degree R**

**1o 1**

**3o 100**

 **A B**

**% yield \_91.75\_\_\_\_\_ \_\_\_8.25\_\_\_\_\_\_**

**For 1o : #1o H\* 1 = 9\*1 =9**

**Fro 3o #3oH \*100 =1\*100 =100**

**sum 109**

**%yield 1o = 100(9/109)=8.25**

**% yield 3o =100(100/109)=91.75**

**\_\_\_\_/12**

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

1. For both SN1 and SN2 substitution of halogens on ROH, what is the common initial intermediate?

 ROH2+ protonated alcohol



1. What name/term is used to describe the position shown here

allylic

\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

1. When addition of HBr across a double bond

adds Br to the side containing the smaller groups=> anti-Markovnikoff\_\_\_\_\_\_addition.

1. What is the order of reactivity for F-, Cl-, Br-, I- when substituting the OH on 1o alcohols ?

 \_\_\_I\_\_\_\_\_> \_\_\_\_Br\_\_\_\_\_\_\_> \_\_\_\_Cl\_\_\_\_\_>\_\_\_\_\_F\_\_\_\_\_\_

 **a**



1. Where does OH go during haloydrin addition on Bob?

 a **b** c d  **b c**

 circle choice(s) above

 **d “Bob”**

1. Whose (variously spelled Russian) rule decides which is the most likely alkene formed from alkyl halides ? \_\_\_Saitzev rule\_\_\_\_\_(Zaitsev)\_\_\_\_\_\_\_\_\_\_
2. In the modern, solution phase reaction of alcohols to alkyl chlorides using pyridine, the common chloride source is the compound: \_\_\_\_SOCl2\_\_\_\_\_\_\_\_\_\_\_\_
3. What solvent is commonly employed in the reaction shown below: \_\_CCl4\_\_\_\_\_\_\_\_\_\_



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

\_\_\_\_\_\_\_\_\_elimination\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

1. What class of reactions leads to bigger alkanes and alcohols?\_organometallic reagent preps\_\_\_\_
2. In the reaction below, clearly identify the substrate (Sub), nucleophile (Nuc) and leaving group (L): (3 pts)



 SUB L NUC

12) Route to larger alkanes \_\_\_\_\_**Corey-House synthesis**\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

13) Route to larger alcohols:\_\_\_\_\_Grignard synthesis\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

\_\_\_/15

##### Mechanisms: Just the Facts (13 pts total)

**In each pair, circle the outcome associated with SN2 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 SN1 halogenation of alcohols (6 pts)**

a) both alcohol and halide affect rate only alcohol affects rate

b) rate limiting step involves 5-coordinate rate limiting step involves 3-coordinate

 complex intermediate

c) rate of reaction increases with non-protic rate of reaction increases with polar protic

 polar solvents solvents

d) works only on 1o alcohols works on 2o and 3o 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)**

#### On speed ( 1 pt each/4 pts total)

Which will react faster assuming HBr/ aqueous w/reflux is applied in each case ?

a) t-butanol or sec-butanol **or ~ same**

b)



 **or ~same**

**c)**



 **or ~same**

**d)**



 **or ~same**

 **Br destabilizes Carbocation**

\_\_\_/21

**Matchmaking (1 pt ea/5 pts total)**

**Match the mechanism to the acronym**  a**cronym** Match from list

1. Mechanism for conversion of ethyl bromide to an ethene \_\_E2\_ Sn 1

b) Mechanism for conversion of CH3Br to CH3NH2: \_SN2\_\_ Sn2

c) Mechanism for bromination of an alkane: \_\_RAD\_\_\_\_\_ E2(elimination)

d) Mechanism for bromination of a 3o alcohol: \_\_SN1\_\_\_\_\_ RAD(free radical)

e) Mechanism involving formation of a racemic mixture \_\_Sn1\_

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

1) racemization = scrambling of molecular handedness T F

2) The reaction of RMgX with H2O 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)**



 **+**



w/pyridine or KHCO3 in solvent

+

neat

isobutanol + Nao



 **ethanol +**

 **+ KOH**



 **+**



 **+**

**\_\_\_/23**



 **Neat or in ether**

**PBr3**(g) +

 **H2O**



 **+ + NaBr**





 **+ 2**



**H2SO4/reflux/NaBr**



#####  +





 …then add







\_\_/16