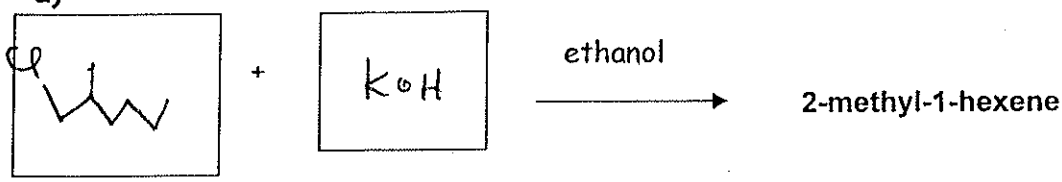
Exam 1: Chemistry 4524 Wednesday 19 February 2014 __/100

Your Name: Answers 1 pt

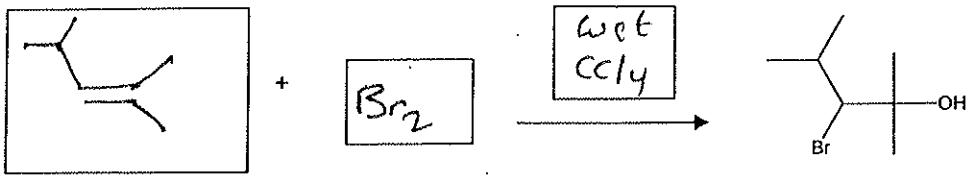
1.1. Boxing with Alkenes (19 pts/1 pt per box)

Fill in the products, reactants and/or conditions for the reactions below

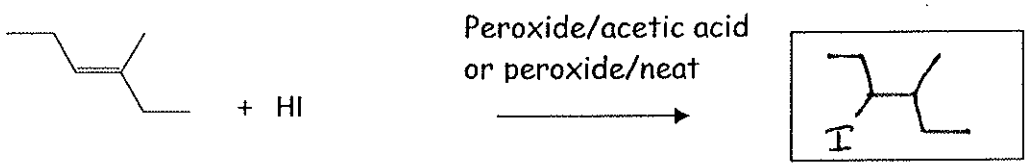
a)



b)

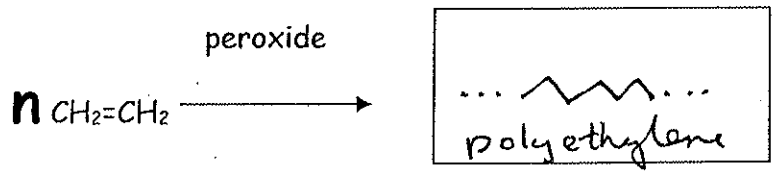


c)

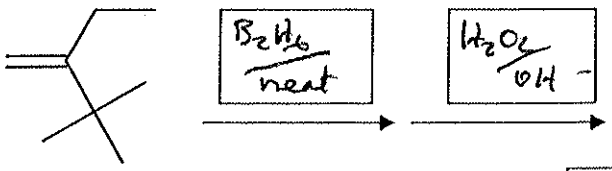


ant: Mark. add.

d)



e)

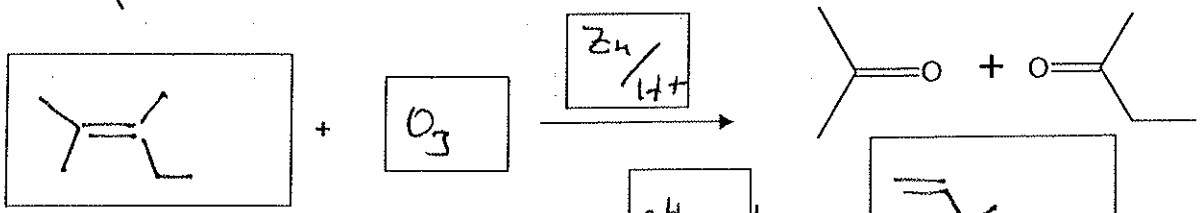


not used

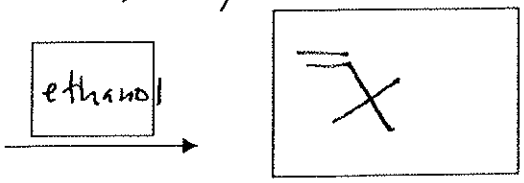
2-ethyl-3,3-dimethyl-1-butanol

(only product; >90% yield in 1 minute

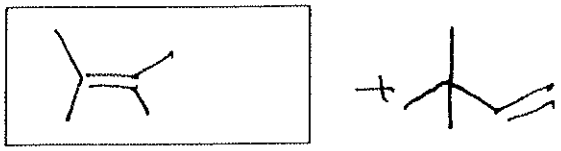
a)



g) 3,3-dimethyl-2-bromobutane + KOH



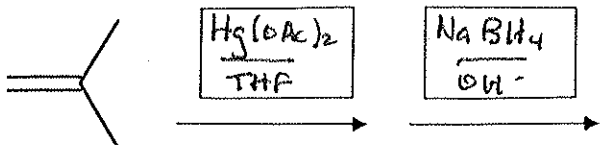
h) 3,3-dimethyl-2-butanol H_2SO_4/reflux



rearrangement

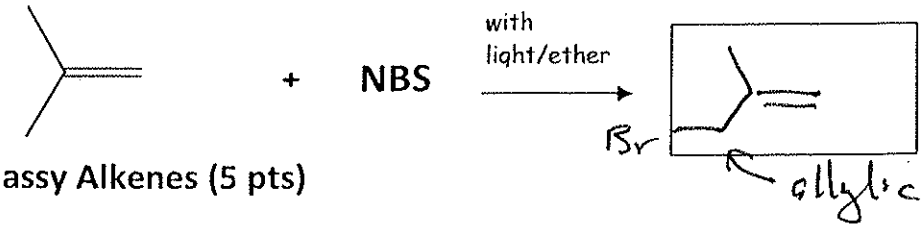
primary cation (minor)

__/16 including name

i) 

Known two-step add. to Markovn. kaff ROH

2-methyl-2-propanol
(only product; >90% yield in 1 minute)

j) 

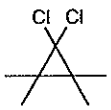
1.2. Classy Alkenes (5 pts)

Classify the reactions written below into one of the alkene reaction categories:

- Carbocation based addition (C+)
- Bridgehead (halohydrin) addition (B)
- Radical-based addition (R)
- Organometallic/redox based addition (O/R)
- Specials (=SP=ozonolysis and allylic substitution)

a) Conc H_2SO_4 + ethylene, then H_2O → ethanol C+

b) NBS + isobutylene → 3-bromo-2-methylpropene Rad or SP

c) $CHCCl_3$ with OH^- + 2,3-dimethyl-2-butene→  Rad

d) Anti-2,3-dibromobutane forms B

e) Anti-diol formed O/R

1.3. Stereo Entertainment Center (37 pts)

1.3.1 Terms of Organic Endearment (12 pts/1 pt each)

1) I'm used to describe a 2 center stereochemical system where the groups of one sort are all on one side like a big E. I sound like urethra, but am spelled differently: Erythro

2) We have adjacent non-equivalent centers but we are the same (e.g. superimposable) even though we are mirror reflections of each other. We are meso compounds (sounds sort of like a Japanese soup base as spoken by a Kansan)

3) Attack on a molecule from opposite sides anti, (bridgehead attack on alkene is an example. Sounds like a relative)

4) Mirror images are not superimposable (rhymes with spiral): chiral

5) Optical activity refers to: (circle your choice)
a) rotation of plane polarized light by a molecular species
b) whether a material absorbs visible light or not
c) whether a compound is cis or trans
d) molecules engaged in naughty, illicit liaisons

6) Letters defining specific handness of sugars, (often confused with + and -): D & L (2 pts)

7) Not mirror images, not superimposable. Chemically and physically different diastereomers

___/16

8) We've got the same formula, same physical properties, but different chemical properties.
We are a(n) enantiomeric pair. Spelling matters *

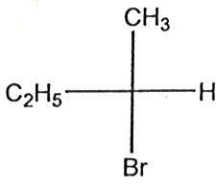
9) Name for a 50:50 mixture of left and righthanded stereo isomers of the same compound: racemic

10) Name for the symbol: α_d^{20} specific rotation (two words, specifically)

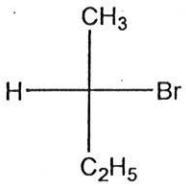
11) Famous French chemist and sometime biologist credited with first recognizing molecular handedness
By growing R and S form of tartaric acid Pasteur (he did the thing with milk !)

1.3.2 One-potato chirality (11 pts)

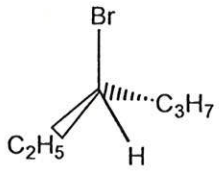
a) Assign the compounds below as R or S (3 pts each/ 9 pts total) Br=81, C=12, H=1



R (S)



R (S)

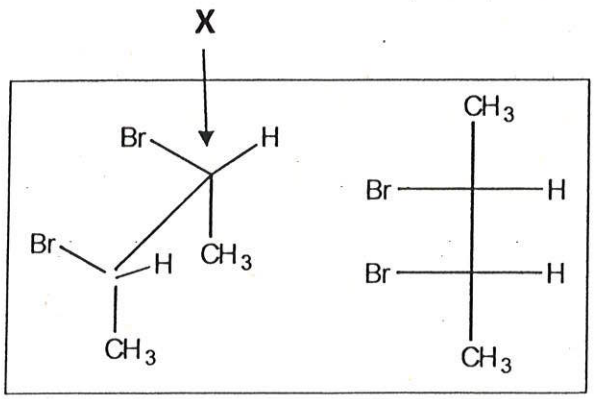


R (S)

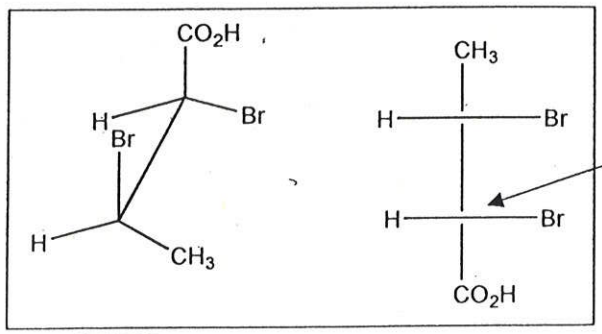
b) Assign the R/S character of the model provided by instructor: (R) S **(circle one. 2 pts)**

1.3.3 Two-potato chirality (14 pts)

a) Determine whether the pair of compounds below are diasteromers, enantiomers or meso structures.
(3 pts each) [circle your answers]



diastereomers enantiomers (meso) *



(diastereomers) enantiomers meso

b) Assign the R/S character of the carbons at X and Y indicated above

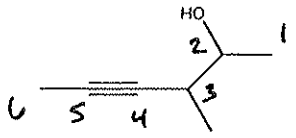
X is: (R) S 4 pts

Y is: (R) (S) 4 pts

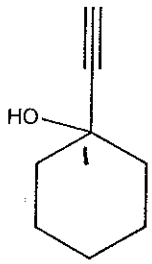
1.4 Alkyne world (39 pts)

1.4.1 Name or draw us! (2 pts each/12 pts total)

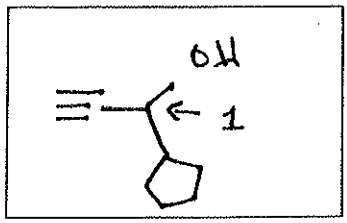
1) C≡C-C-C-Cl 4-chloro-1-butyne (old school) a 4-chloro-but-1-yne

2) 

3-methyl-4-hexyn-2-ol

3) 

1-ethynylcyclohexanol

4) 1-cyclopentyl-2-propyn-1-ol 

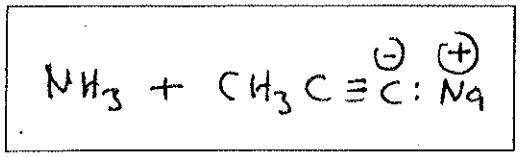
5) C≡C-C-C-OH 3-butyn-1-ol

6) IUPAC name for acetylene ethyne

1.4.2. Alkyne Reactivity (4 pts/2 pts each)

a) Which is the most acidic species? (circle your answer)
H-CH_2CH_3 H-CH=CH_2 H-C≡CH H-C≡C-C-C

b) Predict the product(s) of combining:
$CH_3C{\equiv}CH + NaNH_2$ (in $NH_3(l)$)→



1.4.3. To and from alkynes

1) Write out the classical two-step Bertholet process for synthesis of ethyne (4 pts)

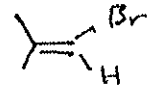
step 1 $CaO + 3C \xrightarrow{1500\text{-}2100^\circ C} CaC_2 + CO$

step 2 $CaC_2 + 3H_2O \longrightarrow Ca(OH)_2 + HC{\equiv}CH$

___/20

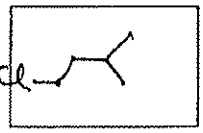
2) Predict the likely product if any (assume R=CH_3) (2 pts each/6 pts total)

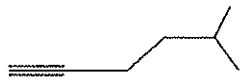
$R_3C\text{-}CH\,Br_2$ —$NaNH_2$ in NH_3(liq)→ NR

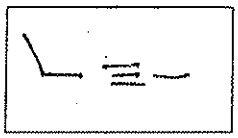
$R_2HC\text{-}CHBr_2$ —$NaNH_2$ in NH_3(liq)→ 

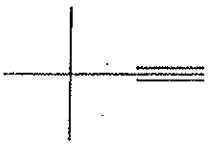
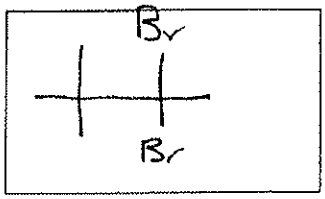
$HC{\equiv}CR$ —$NaNH_2$ in NH_3(liq)→ $Na^+ :\bar{C}\equiv C\text{-}CH_3$

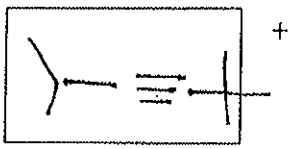
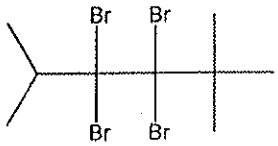
3) **Alkyne Boxing Practice (8 pts/1 pt per box)**

4) $HC{\equiv}CH$ —$NaNH_2$, NH_3→ $NaC{\equiv}CH$ then add 

→ 

 + H_2 —in Pd black (Lindlar)→ 
Only cis form

4)  + 2HBr —heat, a few cons→ 

5)  + 2 Fill in # Br_2 → 

1.4.4. Mini-Road map trip (5 pts)

Starting from ethene and ethyne, suggest a route to 3-hexyne