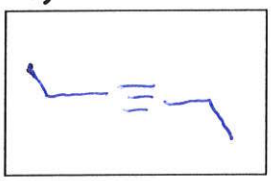
Exam 1: Chemistry 4524 24 Feb 2017 __/100

Your Name: Answers

1.1. Boxed and Addled by Alkenes (23 pts/1 pt per box)

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

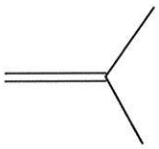
a)



+ H_2 — Pd Black (Lindlar's catalyst) → Z only 3-hexene

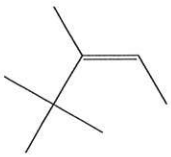
b) propene + CH_2N_2 — Light & Cu^0

c)

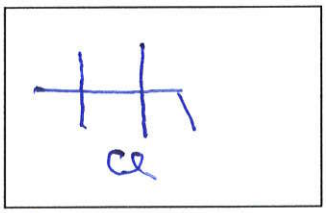


+ HBr — H_2O_2 → in glacial acetic acid → 2-methyl-1-bromo-propane (mostly)

d)

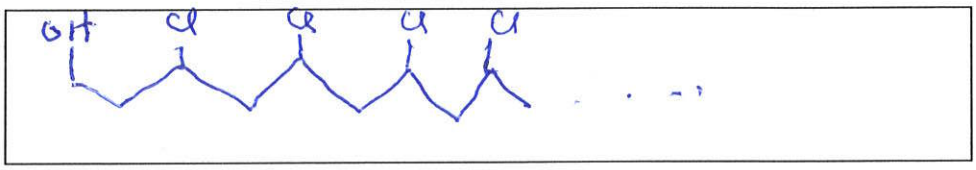


+ HCl — glacial acetic acid, no peroxides →



e) peroxide

n CH_2=$CHCl$ →

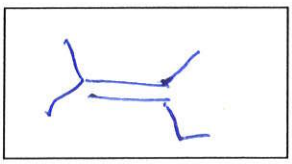


f)

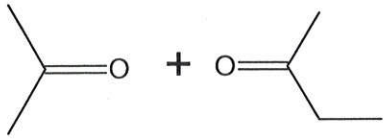
$Hg(OAc)_2$ / THF → $NaBH_4$ / OH^- → 2-ethyl-3,3-dimethyl-2-butanol

(only product; >90% yield in 1 minute

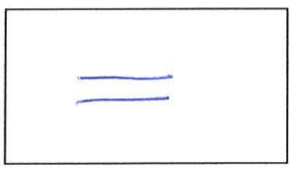
g)



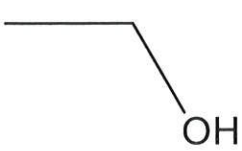
O_3 → Zn / H^+ →



h) Industrial route to ethanol



H_2SO_4 (conc) → H_2O →



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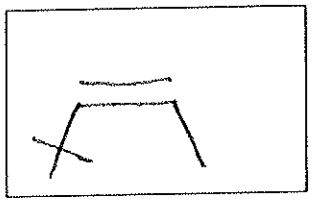
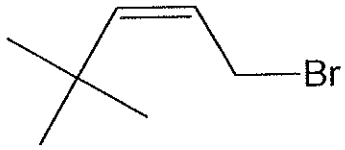
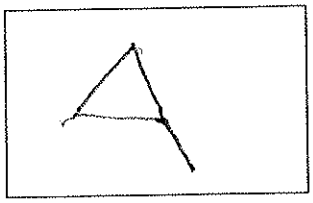
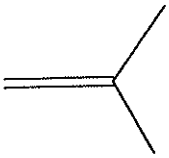
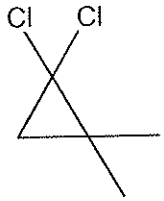
i)  + NBS → (uv light) 

j)  +CH_2I_2 → ($Zn(Cu)$) 

k)  + $CHCl_3$ + OH^- → 

1.2. Stereo Entertainment Center (35 pts)

1.2.1 Terms of Organic Endearment (15 pts/1 pt each)

1) I'm used to describe a 2 center stereochemical system where the groups of one sort are all on opposite sides. I sound almost religious but for my 'r': threo

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 an alkene from the same side: Syn (sounds like something you should not do mispelled.....)

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 and amino acids (Doc hates this one): D & L (2 pts)

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

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

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) Letter used by the Ingold-Cahn-Prelog system to indicate left handedness S (~ evil)

12) Attack on an alkene that occurs during halohydrin formation: anti (sounds like a relative)

13a) German word associated with R Rechts 13b) German word associated with Z Zusammen

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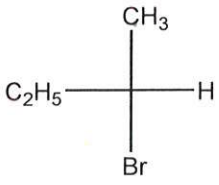
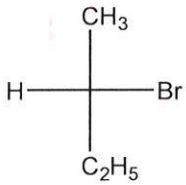
1.2.2 One-potato chirality (6 pts) Can use kits provided

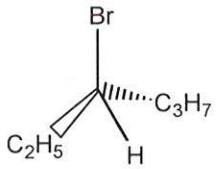
a) Assign the compounds below as R or S (2 pts each/ 6 pts total) Br=81, C=12, H=1



R (S)



R (S)

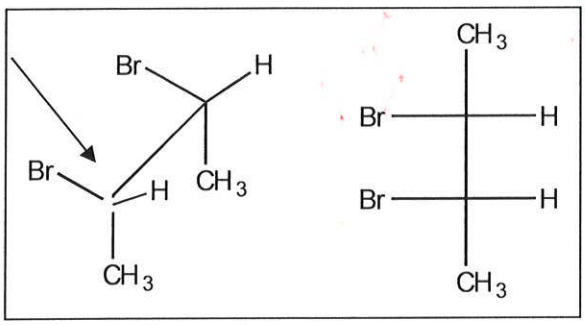


R (S)

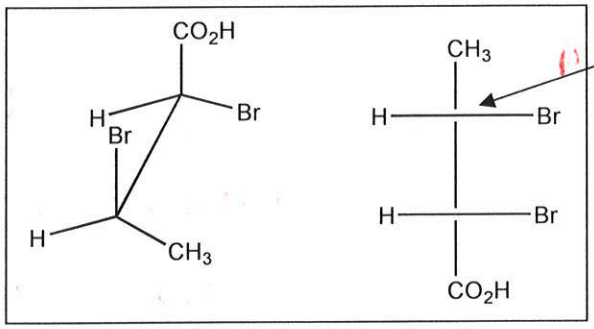
1.3.3 Two-potato chirality (11 pts) Can use kits provided

a) Determine whether the pair of compounds in the boxes below are diasteromers, enantiomers or meso structures. (2 pts each) [circle your answers]

X



diastereomers enantiomers (meso)



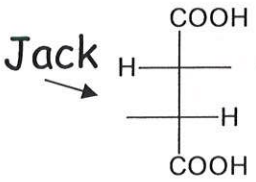
Y

(diastereomers) enantiomers meso

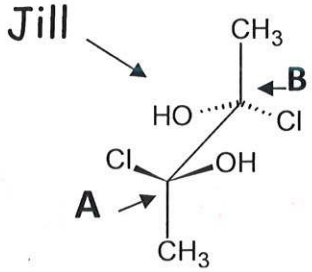
a) Assign the R/S character of the carbons at X and Y indicated above

X is: R (S) 2 pts

Y is: R (S) 2 pts



Jack is: a) Z b)E c) D (d) Threo e)syn f)poop



Jill is : a) Threo (A=S,B=S) (b) Meso (A=R S,B=S R)

c) Z, A=R, B=S) d) Erythro , A=S, B=S) 2 pts

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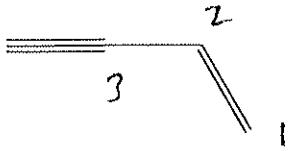
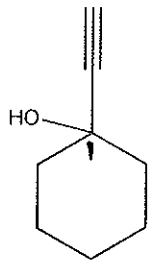
1.3 Alkyne world (40 pts)

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

1) C≡C-C-C-Br — 5-bromo-1-pentyne

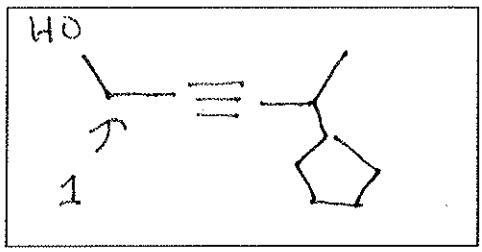
2) 

1-buten-3-yne

3) 

1-ethynylcyclohexanol

4) Draw 4-cyclopentyl-2-pentyn-1-ol



5) C≡C-C-C-OH — 3-butyn-1-ol

6) IUPAC name for acetylene — ethyne

1.3.2. Alkyne Reactivity (2 pts/1 pt 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 $NH_3(l)$)→ $CH_3-C{\equiv}C^-Na^+ + NH_3$

1.3.3. To and from alkynes

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

step 1 $3C(s) + CaO(s) \xrightarrow{1800^\circ C} CaC_2(s) + CO(g)$

step 2 $CaC_2(s) + 2H_2O \longrightarrow Ca(OH_2)(aq) + HC{\equiv}CH(g)$

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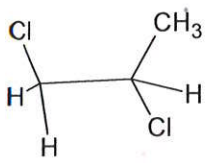
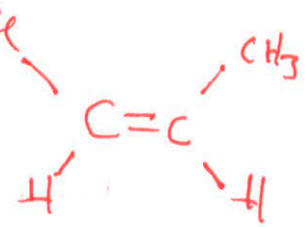
2) Predict all the likely products if any: (1 pt each/5 pts total)

CH_3-$CH\ Br_2$ $\xrightarrow{NaNH_2 \text{ in } NH_3(liq)}$ $HC\equiv CH$

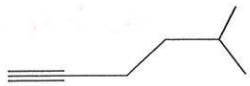


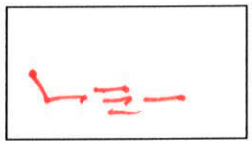
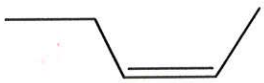
$\xrightarrow{NaNH_2 \text{ in } NH_3(liq)}$ 1) $H-C\equiv C-CH_3$ 2) 

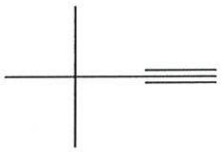
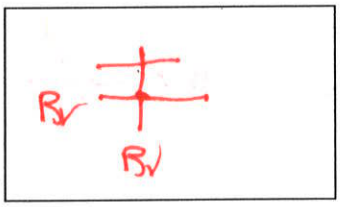
(show all three possible) 3) $CH_2=C(CH_3)(Cl)$

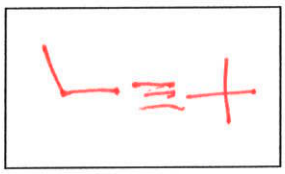
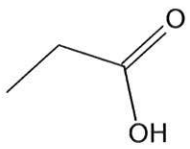
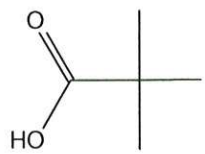
Cl-$C\equiv C$-Cl $\xrightarrow{NaNH_2 \text{ in } NH_3(liq)}$ NR

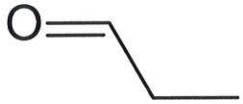
3) Alkyne Boxing Practice (20 pts/1 pt per box)

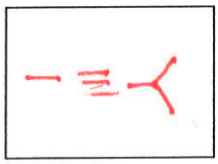
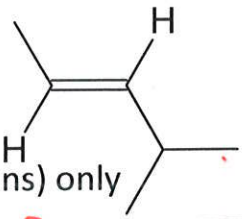
4) $HC\equiv CH$ $\xrightarrow{NaNH_2/NH_3}$ $HC\equiv C^-Na^+$ then add  

 + H_2 $\xrightarrow{Pd\ black\ (Lindlar)}$  Only cis form

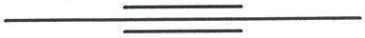
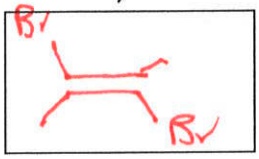
4)  + 2HBr $\xrightarrow[\text{Solvent ?}]{\text{glacial acetic acid}}$ 

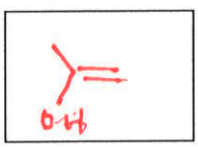
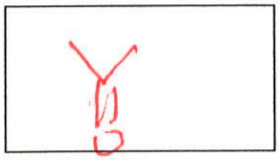
5)  $\xrightarrow{O_3}$ $\xrightarrow{H^+/Zn}$  + 

6)  $\xrightarrow{B_2H_6}$ $\xrightarrow{OH^-/H_2O_2}$ 

7)  + NH_3 $\xrightarrow{Na^0}$ 

E(trans) only

8) Br_2 +  $\xrightarrow[\text{solvent}]{CH_2Cl_2 \text{ or } CCl_4}$  indicate Stereochemistry trans (E)

9) H_2O +  $\xrightarrow[H_2SO_4]{HgSO_4}$  then shifts to... 

enol keto

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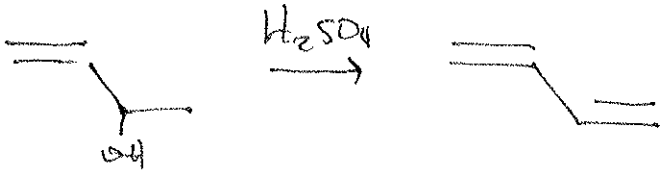
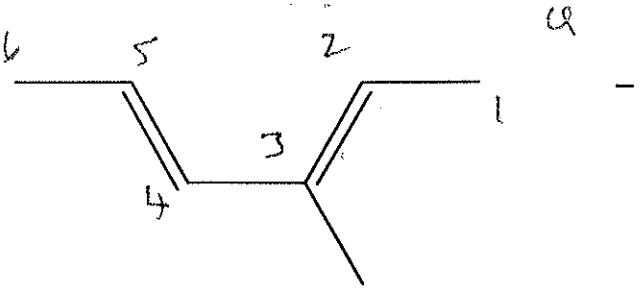
1.4. Basic Alkadiene Finishing Touches (6 pts)

1) Name (0r provide examples) of two different routes to alkadienes:

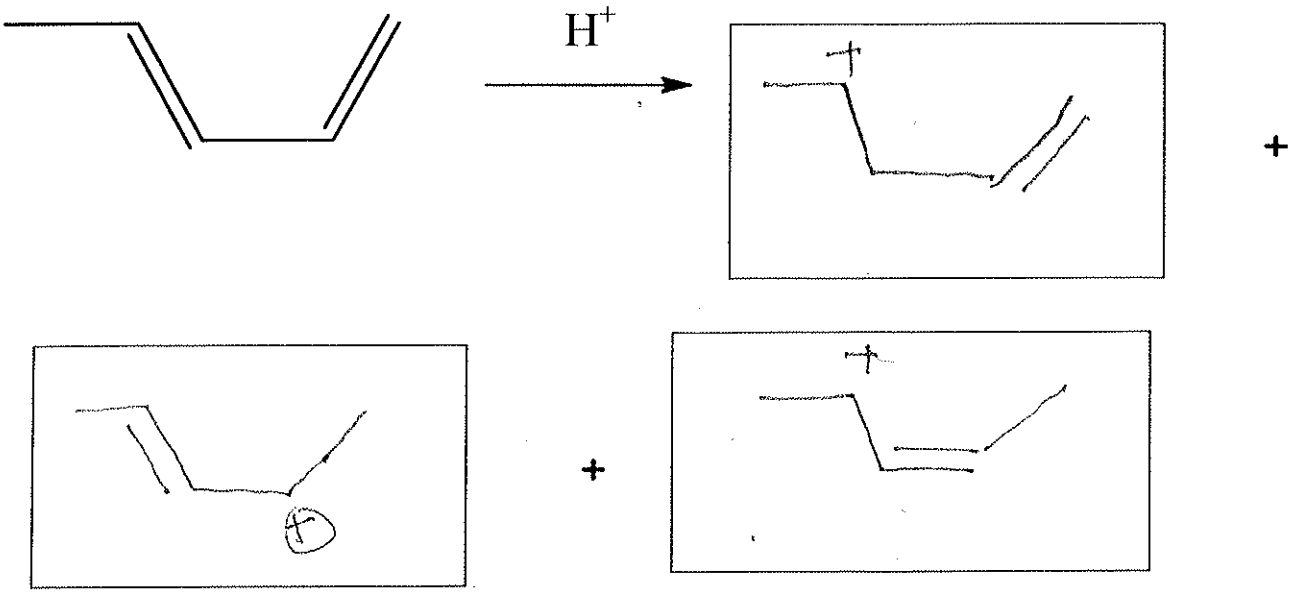
a) dehydration : 

b) dehydrohalogenation 

2) Name me: 

3-methyl-2,4-hexadiene
(IUPAC)

3) Draw the three possible carbocations formed when the diene below reacts with H^+:



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