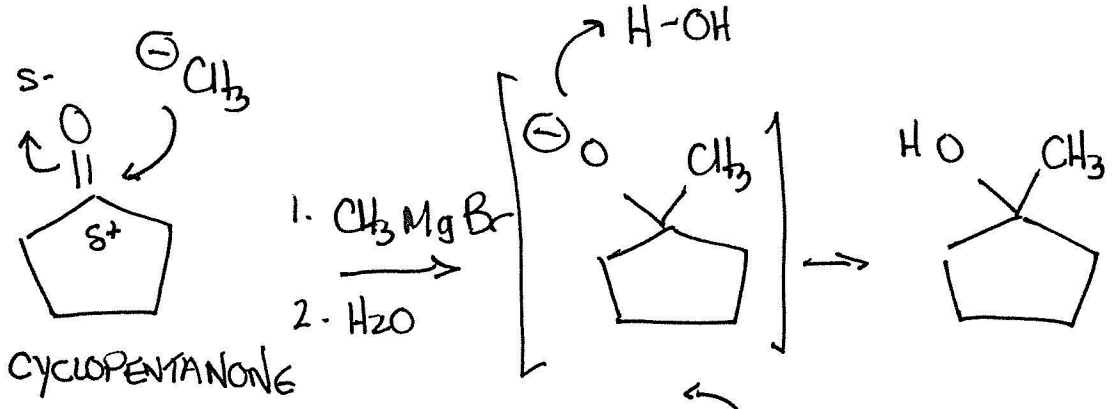
PROBLEM SET #20
SOLUTIONS

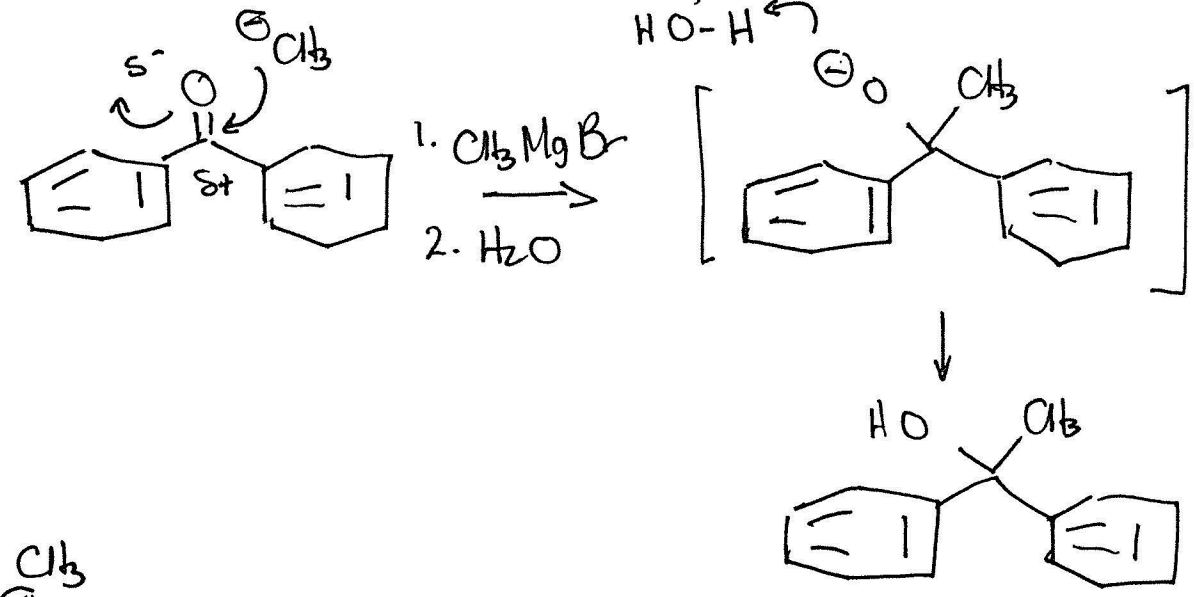
17.9

a)



CYCLOPENTANONE

b)



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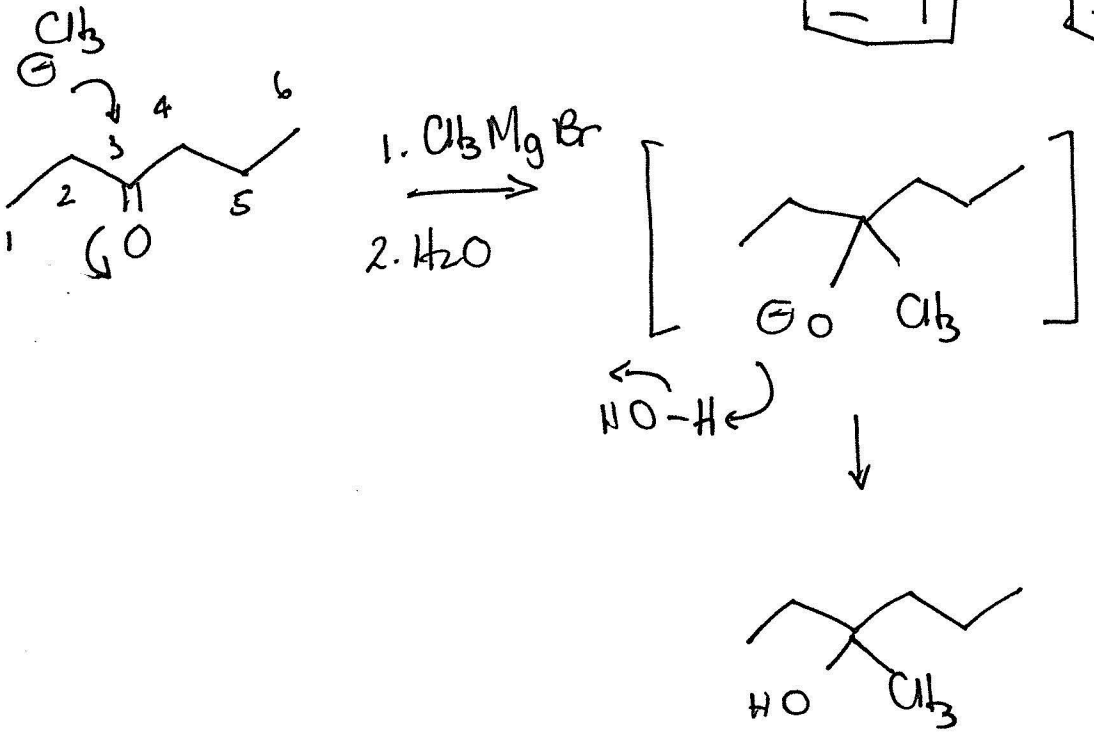
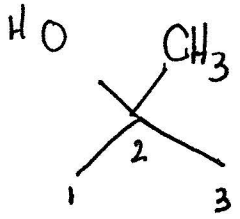
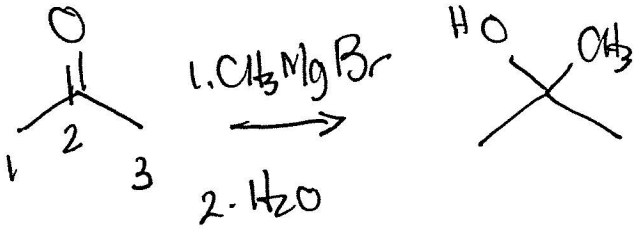


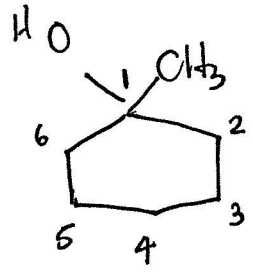
17.10

a) 

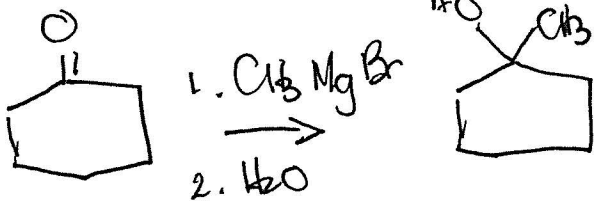
2-methyl-2-propanol

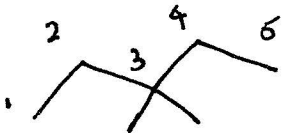
The carbon atom bonded to the hydroxyl group (OH) of the alcohol must be the carbonyl carbon of the starting material.



b) 

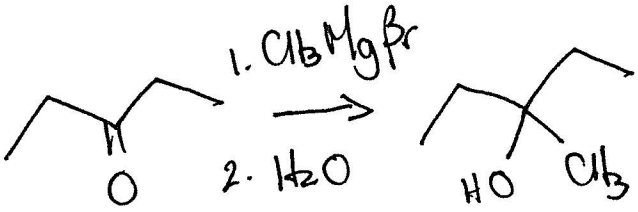
1-methylcyclohexanol

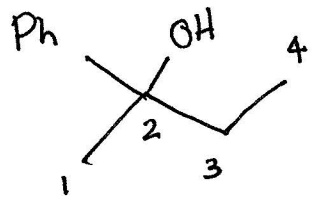


c) 

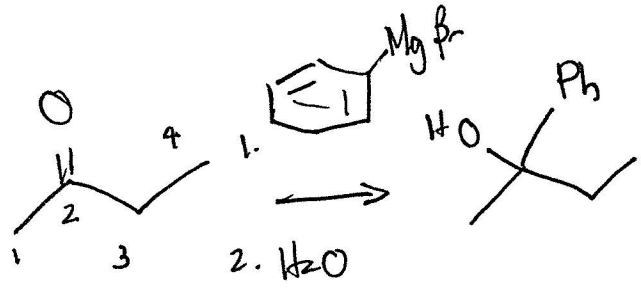
HO CH3

3-methyl-3-pentanol



d) 

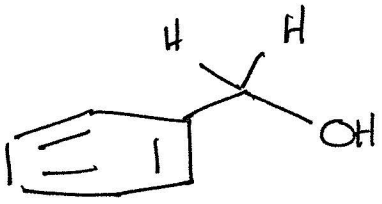
2-phenyl-2-butanol



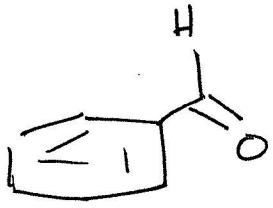
= Ph

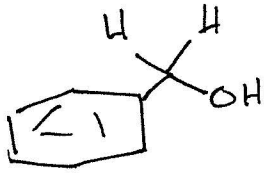
17.10 (cont'd)

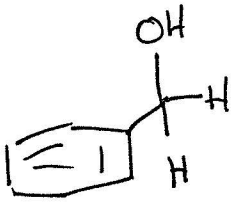
e)



BENZYL ALCOHOL







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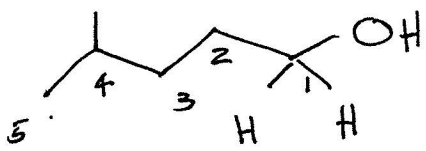
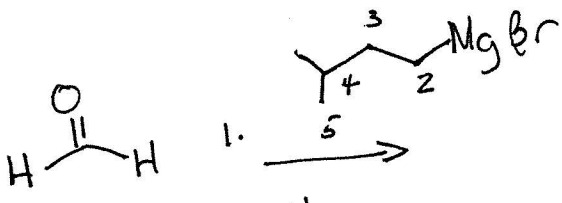
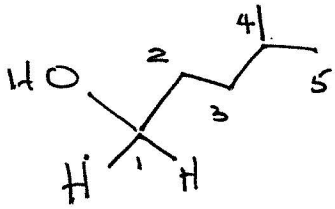


4-methyl-1-pentanol





17.30

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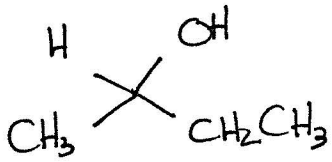
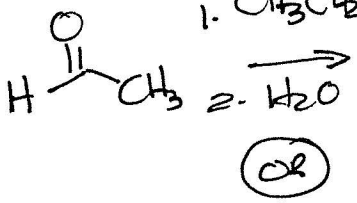
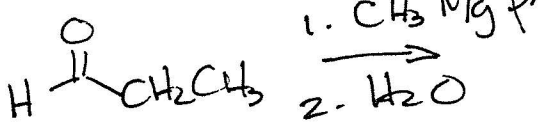
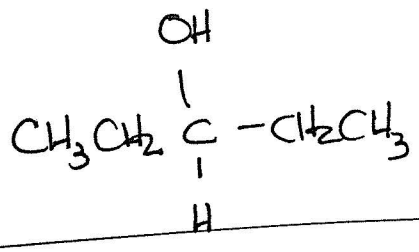


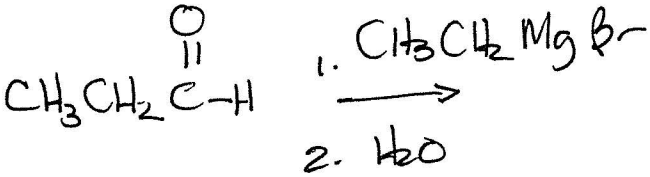


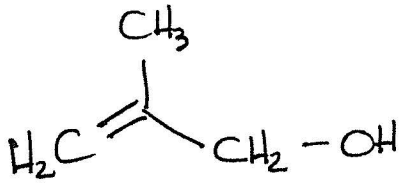
(or)

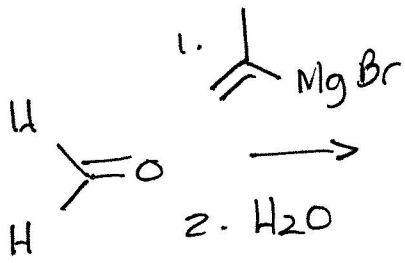


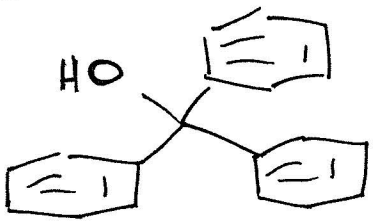
17.30

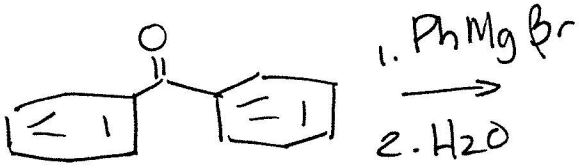
b) 

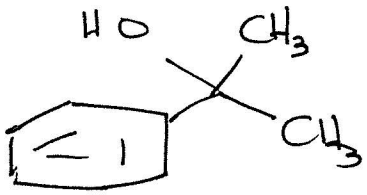


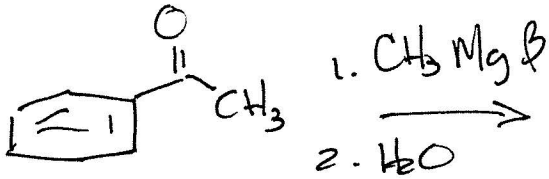
c) 



d) 



e) 



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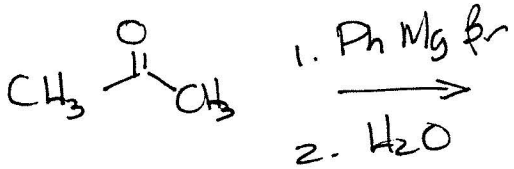
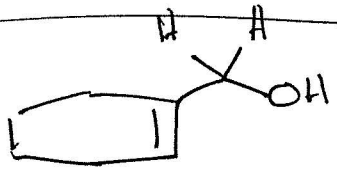
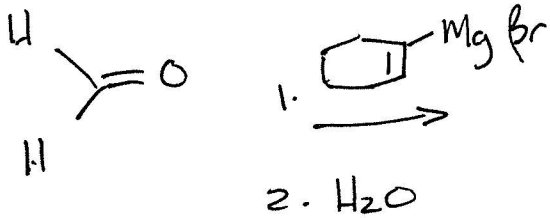
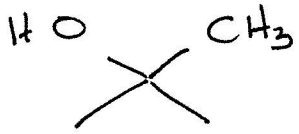


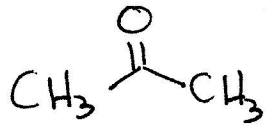
f) 



17.32

a) 2-methyl-2-propanol





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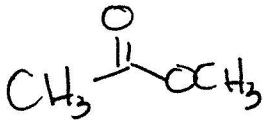

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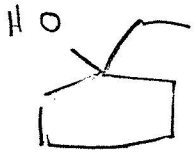
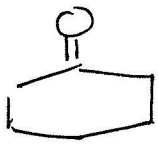
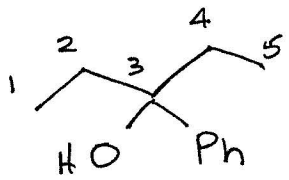
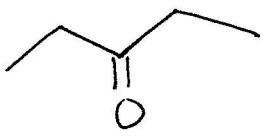




1. CH_3CH_2MgBr
2. H_2O

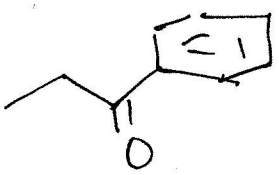
c)





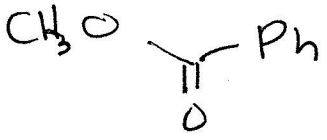
1. $PhMgBr$
2. H_2O

OR



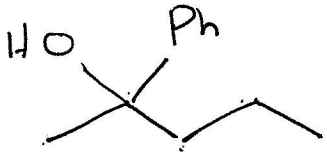
1. CH_3CH_2MgBr
2. H_2O

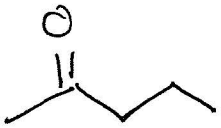
OR



1. 2 equivs CH_3CH_2MgBr
2. H_2O

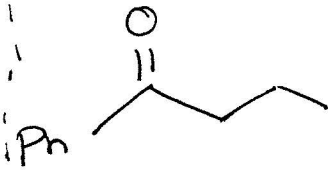
17.32 (cont'd)

d) 



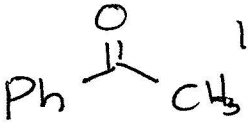
1. $PhMgBr$
2. H_2O

OR



1. CH_3MgBr
2. H_2O

OR



1. $CH_3CH_2CH_2MgBr$
2. H_2O

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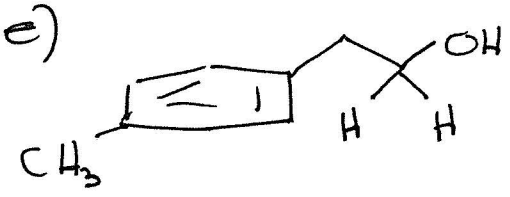
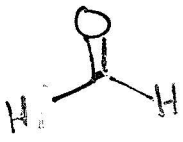
e) 



1. 
2. H_2O

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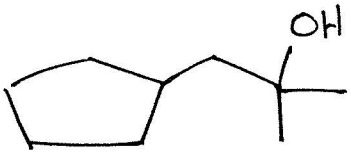
f) 

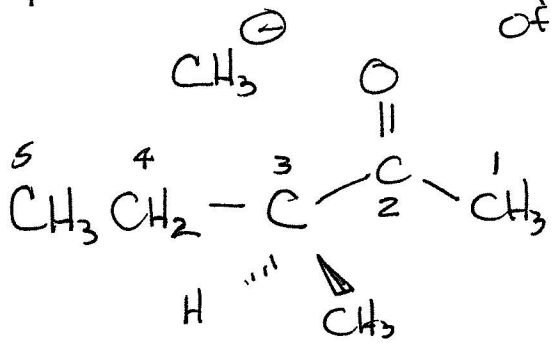
1. CH_3MgBr
2. H_2O

OR

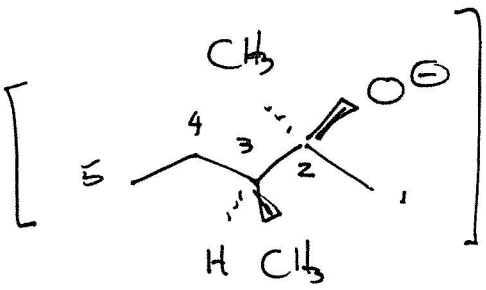
1. 
2. H_2O

17.54

The Grignard reagent can react from the top face + botton face of the sp^2 carbonyl

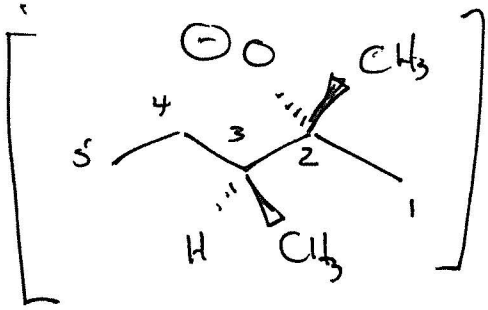


5-3-METHYL-2-PENTANONE



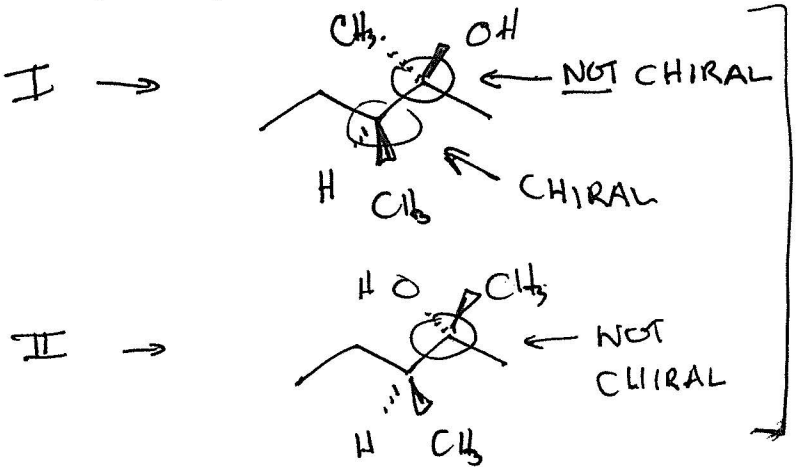
I. (BOTTOM)

The C_3 carbon is CHIRAL and is NOT affected by reaction w/ CH_3MgBr (Methyl magnesium bromide)



II. (TOP)

Each of the tetrahedral intermediates (I ; II) react w/ $H^{\oplus}$ (acidification)

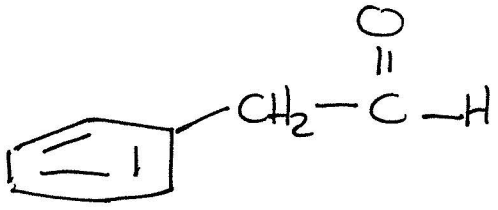


These are the SAME compound.

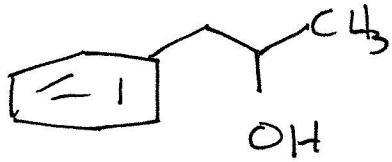
So ONLY 1 Product forms as a pure stereoisomer

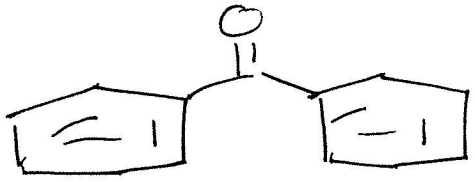
It is OPTICALLY Active.

19.34d

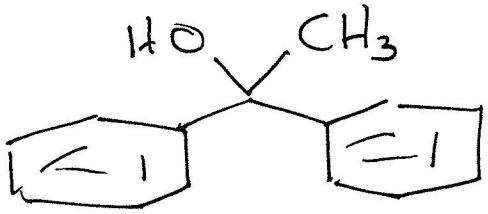
d) 

Phenyl acetaldehyde

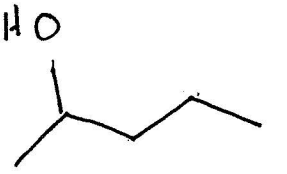


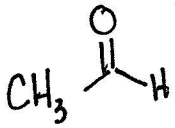


1. CH_3MgBr
2. $H_3O^{\oplus}$



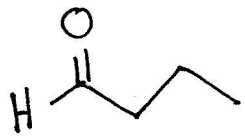
19.36

a) 



1. $CH_3CH_2CH_2MgBr$
2. H_2O

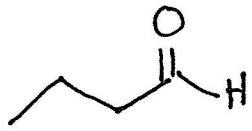
OR



1. CH_3MgBr
2. H_2O

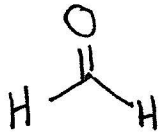
19.36 (cont'd)

b)



$NaBH_4$

CH_3OH

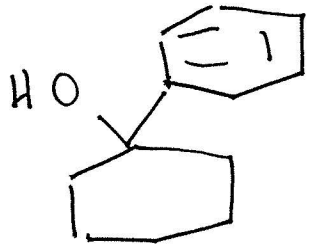


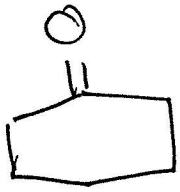
1. $CH_3CH_2CH_2MgBr$

2. H_2O

---

c)



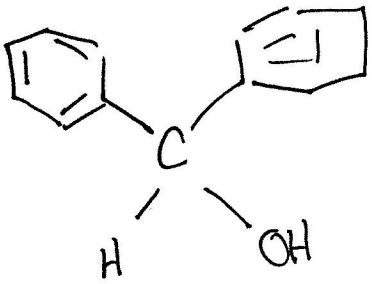


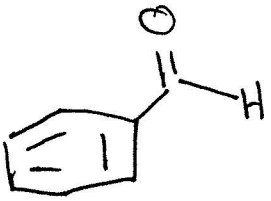
1. $PhMgBr$

2. H_2O

---

d)

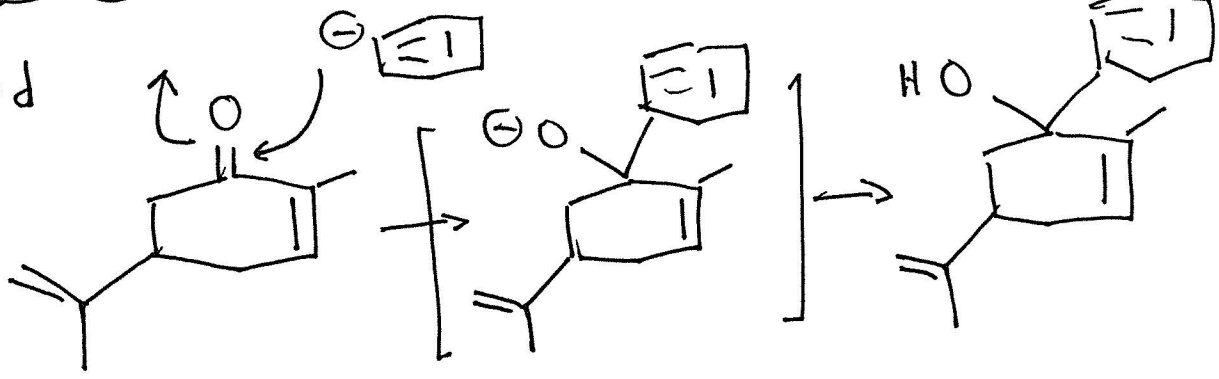




1.

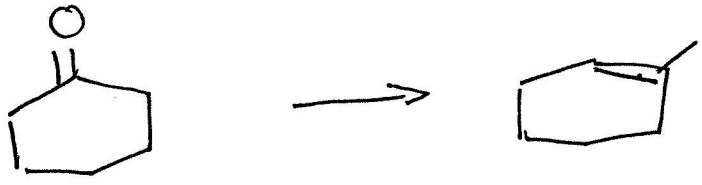
2. H_2O

19.40 d



19.41 CYCLOHEXANONE → 1-METHYLCYCLOHEXENE

a)



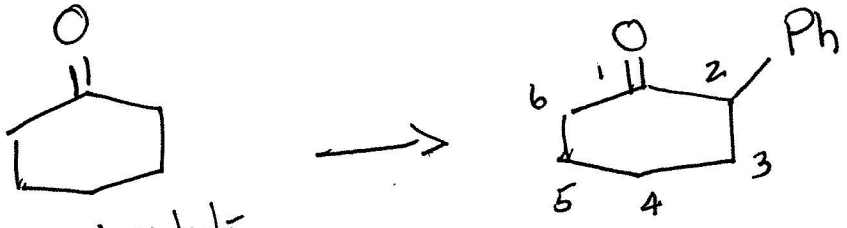
1. $LiN(iPr)_2$
2. CH_3I

H_3O^+ or $POCl_3$, Et_3N (E_1 or E_2)

$NaBH_4$, CH_3OH

---

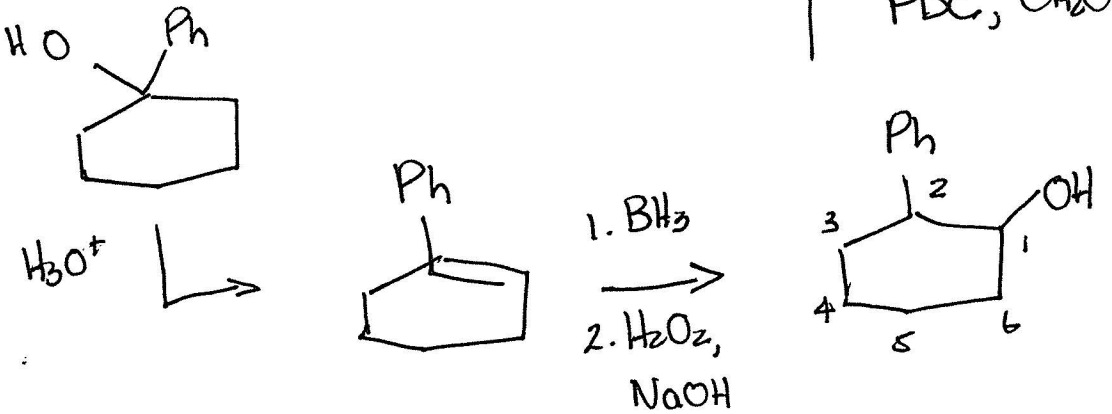
b)



CYCLOHEXANONE → 2-Phenylcyclohexanone

1. $PhMgBr$
2. H_2O

PCC or PDC, CH_2Cl_2

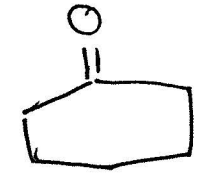


H_3O^+

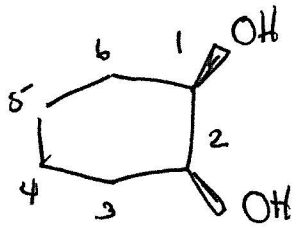
1. BH_3
2. H_2O_2, $NaOH$

19.41 (cont'd)

c)



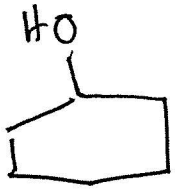
CYCLOHEXANONE



cis- 1,2-cyclohexanediol

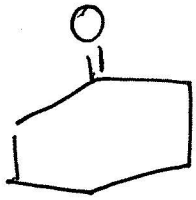
$\downarrow$ $NaBH_4$, CH_3OH

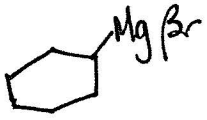
$\uparrow$ $KMnO_4$



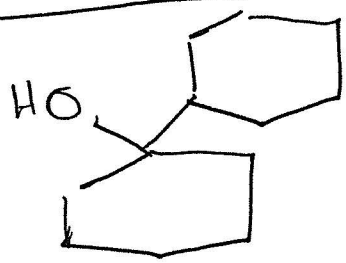
H_3O^+ or $POCl_3$, Et_3N

d)



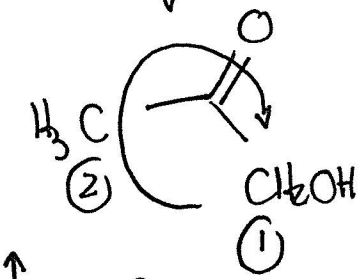
1. 

2. $H_3O^{\oplus}$



5.23a.

RE



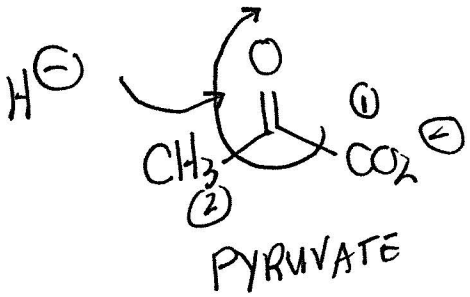
CLOCKWISE

$\uparrow$ S1

S1

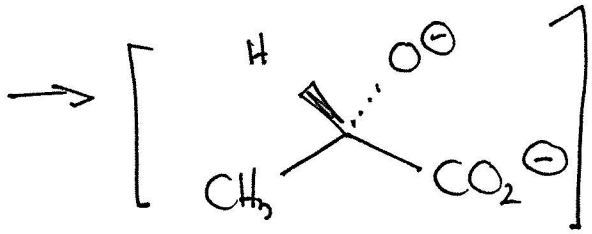
1. orient the molecule so substituents around the carbonyl have a CLOCKWISE ORDER.
2. Attack from top is RE
3. Attack from bottom is S1

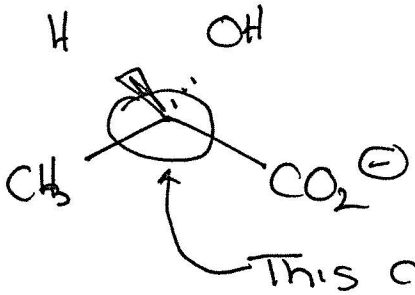
5.24.



PYRUVATE

Attack from front (top) RE





This carbon is chiral.

To determine the STEREOCHEMISTRY (i.e. R or S absolute configuration)

first determine the priorities of the substituents around the chiral center.

H- ④

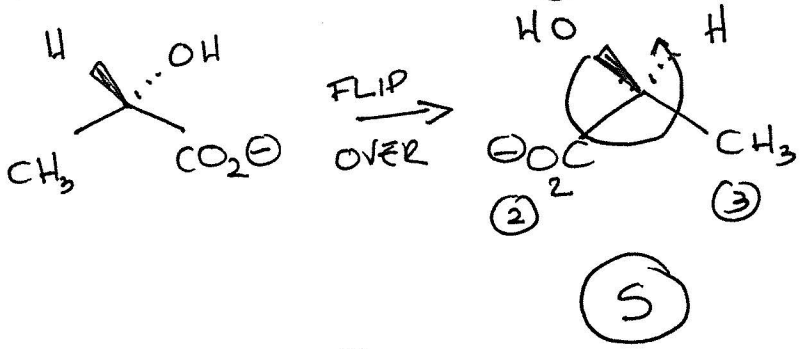
HO- ①

$-CH_3$ ③

$-CO_2^{\ominus}$ ②

Substituent of LOWEST priority (i.e., H) must be in back

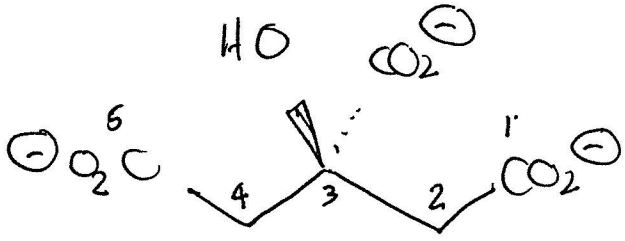
flip molecule over to get substituent of lowest in BACK



(S)

Product has (S) configuration.

5.59

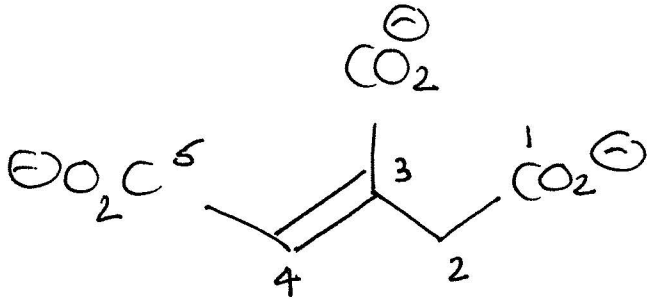


For dehydration to occur the "leaving group" (OH) must be trans to H on adjacent carbon.

(E2 Elimination requires trans or Anti periplanar orientation of H and LG)

There are two H on C_2 and two H on C_4. Both C_2 and C_4 are PROCHIRAL

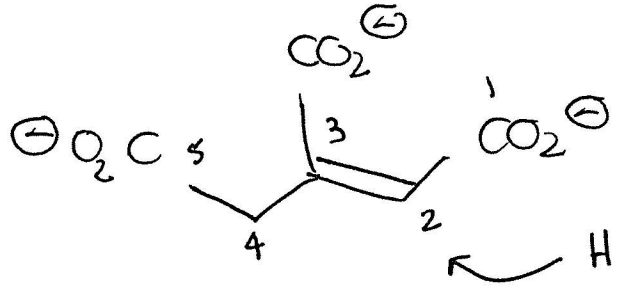
If dehydration occurs at C_4, the product is:



H "lost" from C_4

5.59 (cont'd)

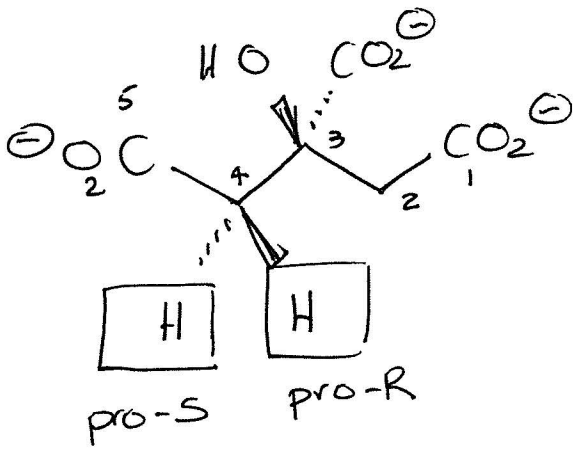
If dehydration occurs at C_2, the product is



This is the product derived from pro-R route.

C_4

Each H on prochiral C_4 can be designated as pro-R or pro-S.

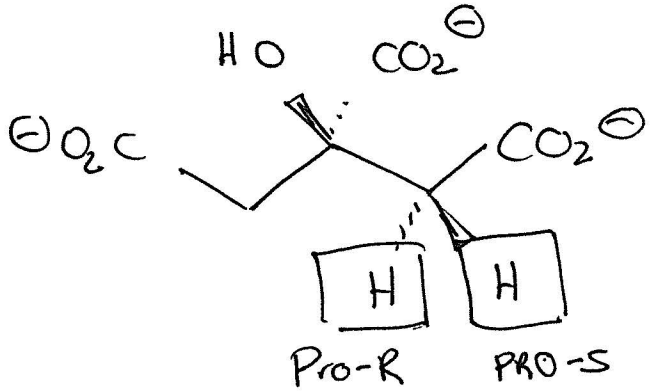


The H atom at C_4 that is TRANS to the OH is the reactive H in the dehydration (E_2 elimination)

This H is the pro-S hydrogen.

C_2

Each H on prochiral C_2 can be desgnated as pro-R or pro-S



The H atom at C_2 that is TRANS to the OH is the reactive H.

This is the pro-R hydrogen