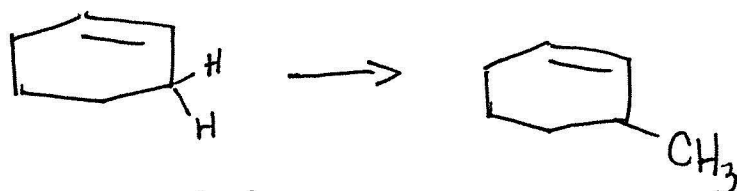
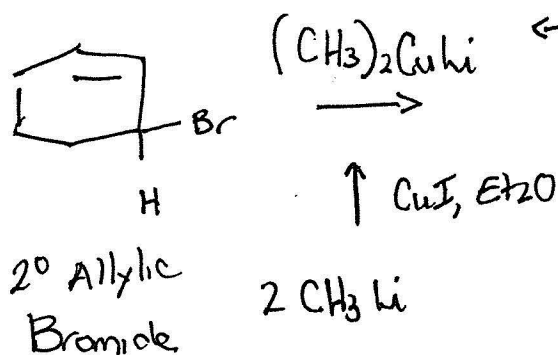


10.11

a)

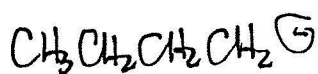
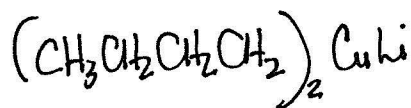
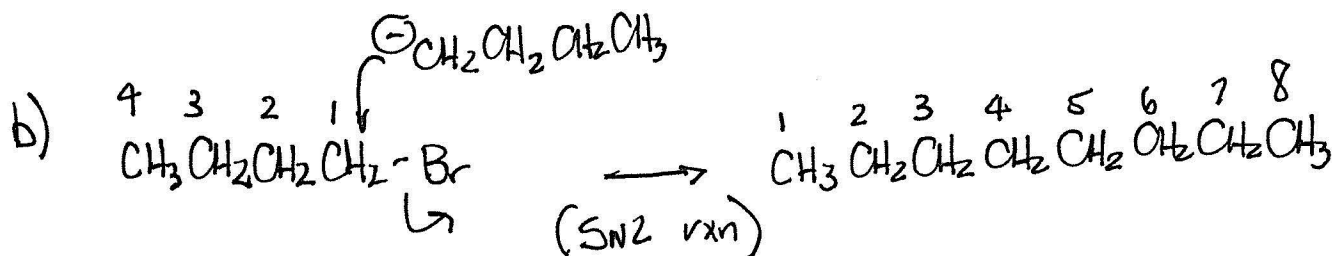
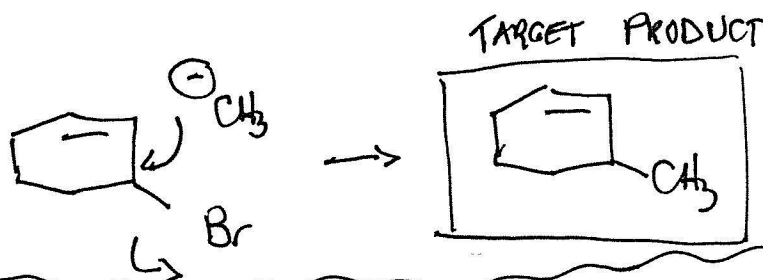


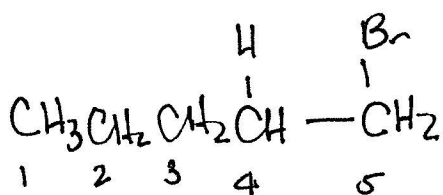
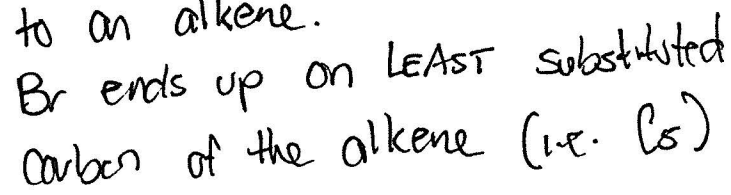
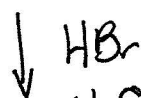
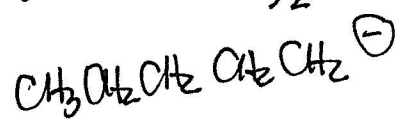
NBS, $h\nu$
(allylic bromination)



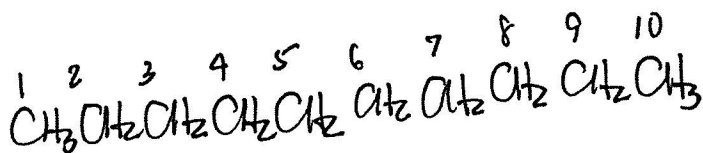
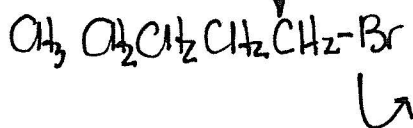
The dimethyl lithium cuprate reacts w/ the allylic bromide in an S_N2 reaction.

$(CH_3)_2CuLi$ is the equivalent of CH_3^- . CH_3^- is the nucleophile in the S_N2 reaction.

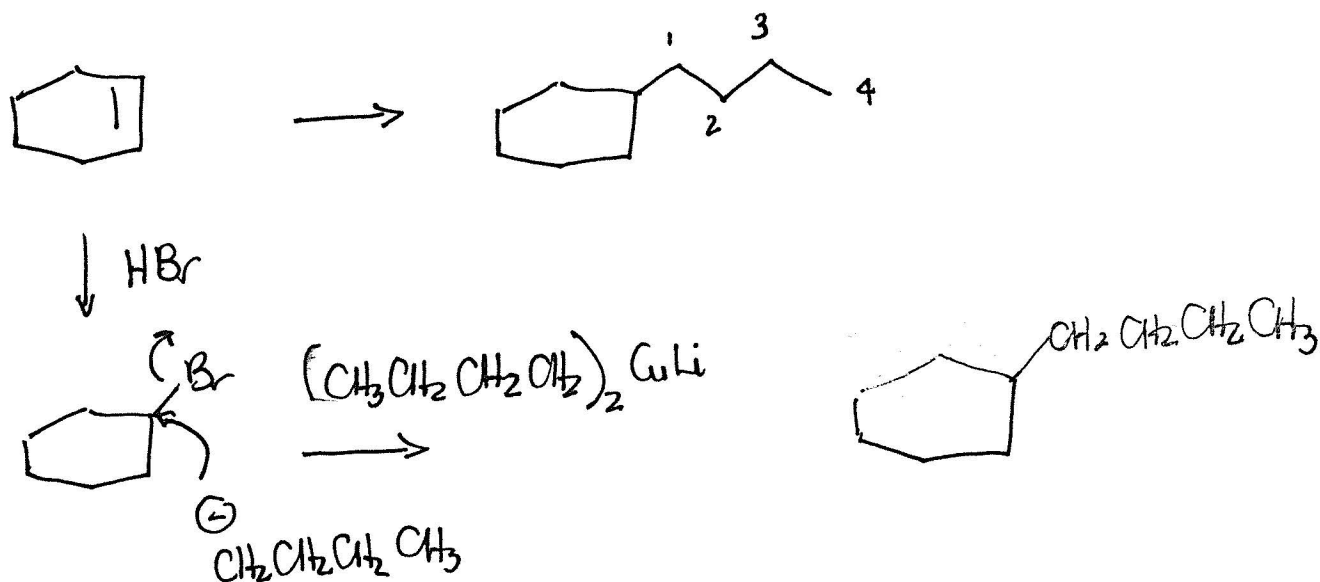



$$(CH_3CH_2CH_2CH_2CH_2)_2 CuLi$$


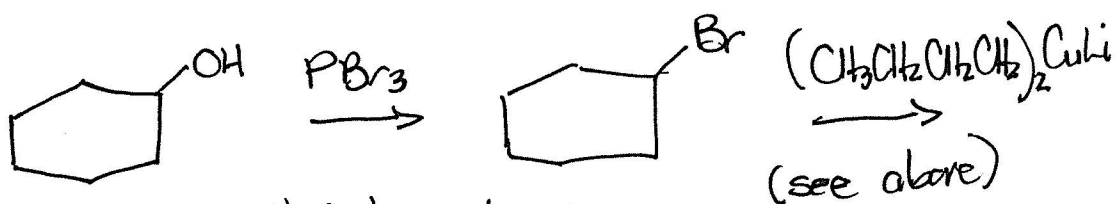
is the Nu:



10.34



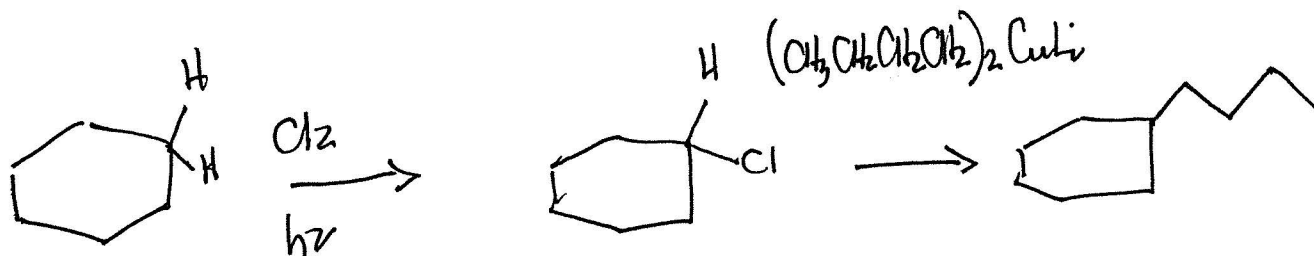
The dibutyl lithium cuprate acts as Nu:
 in an $\text{S}_\text{N}2$ reaction
 with the 2° alkyl
 bromide. The 2° alkyl
 bromide is generated from
 the alkene w/ HBr in
 an electrophilic addition



The 2° alkyl bromide can
 be generated from the 2°
 alcohol with PBr_3



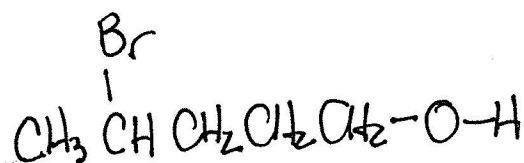
10.34 (cont'd)



Reaction of an alkane with Cl_2 in the presence of UV light results in radical chlorination to give an alkyl chloride

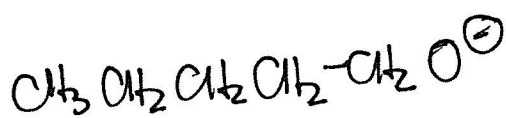
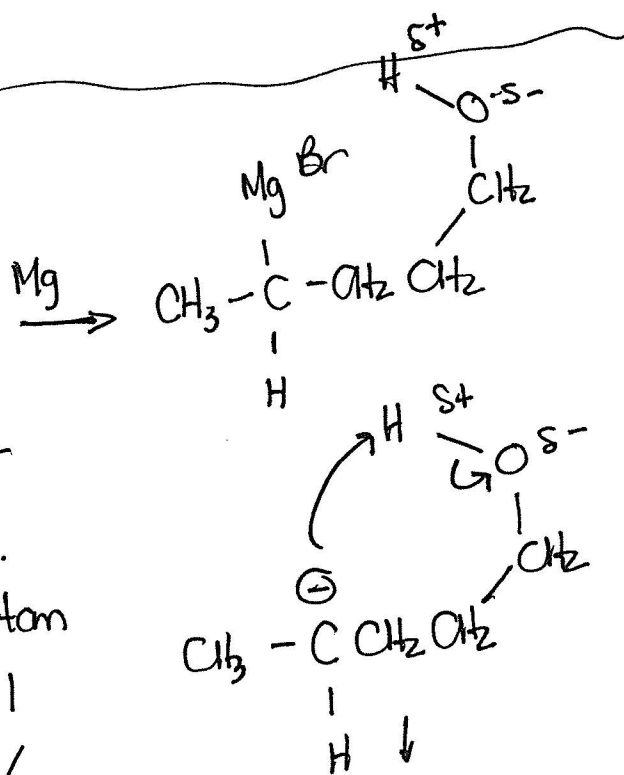
This alkyl chloride then reacts with dibutyl lithium cuprate to give butyl cyclohexane as shown in the previous 2 examples

10.36



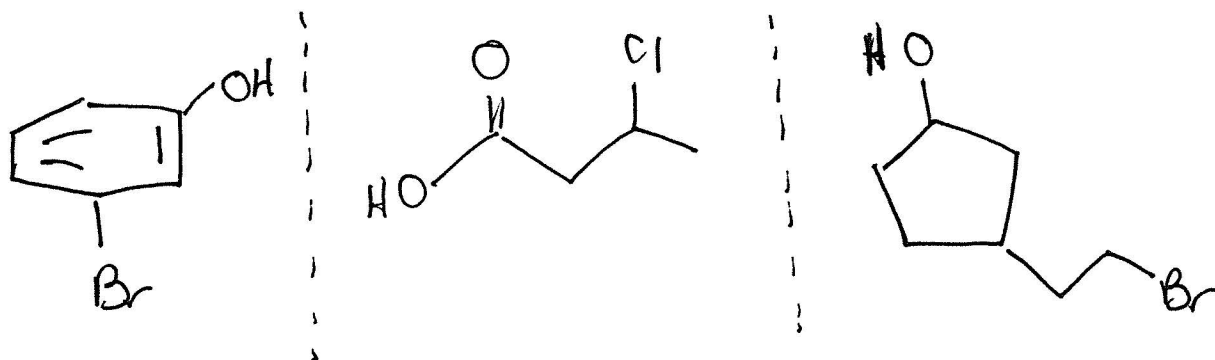
4-bromo-1-pentanol

contains a protic functional group (i.e. alcohol). The H atom of the alcohol will immediately react w/ a Grignard reagent generated from the alkyl bromide part of the molecule.

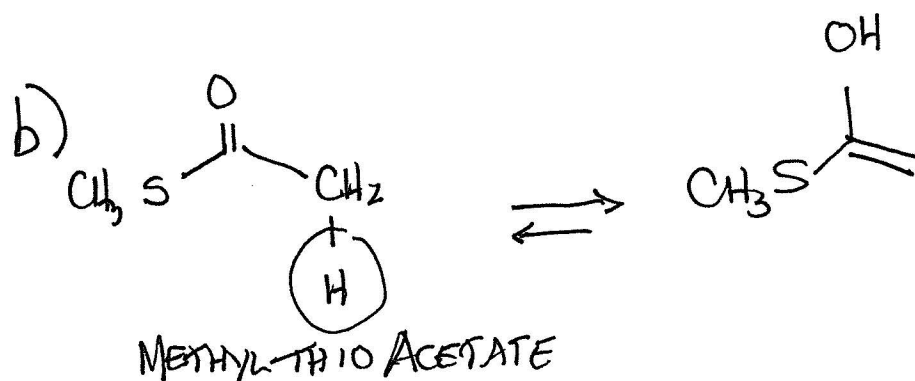
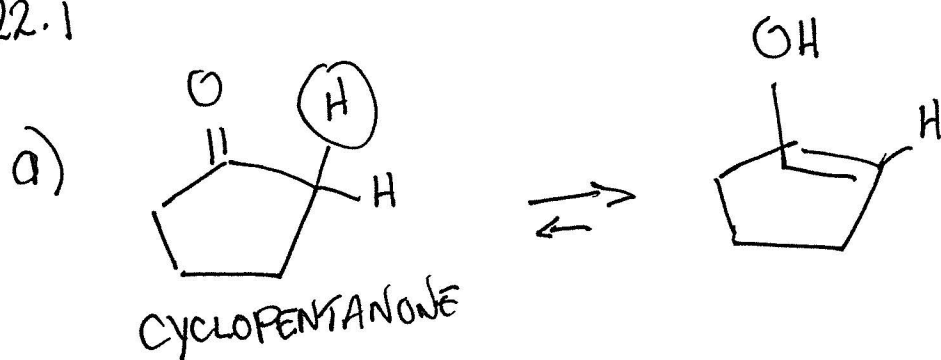


10.36 (cont'd)

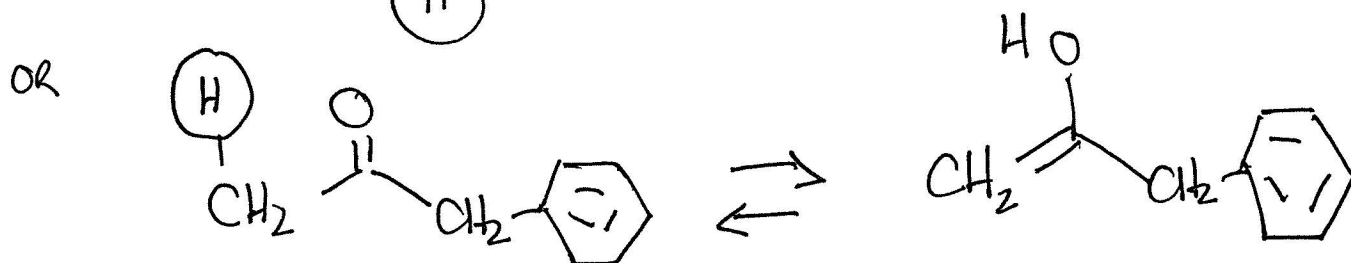
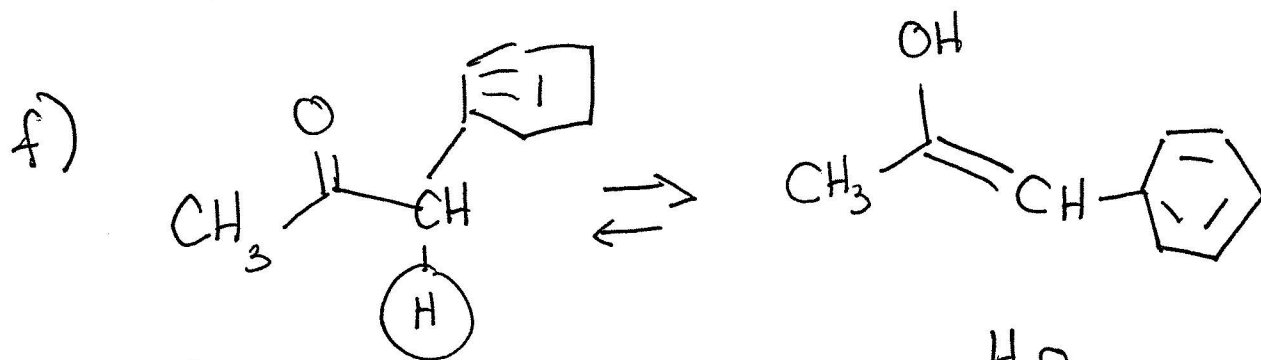
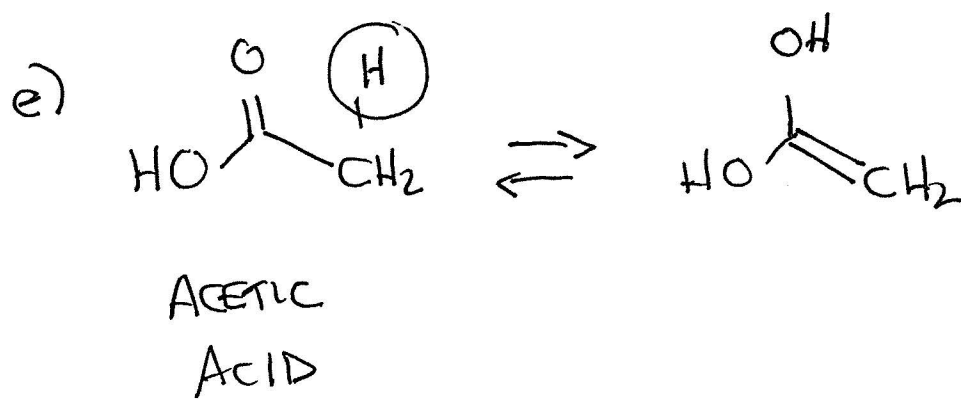
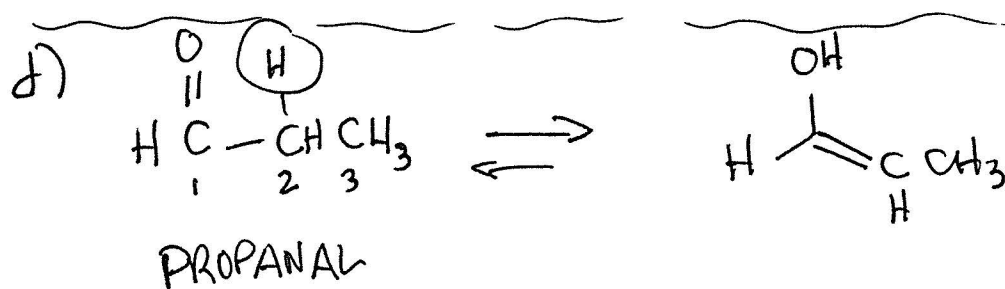
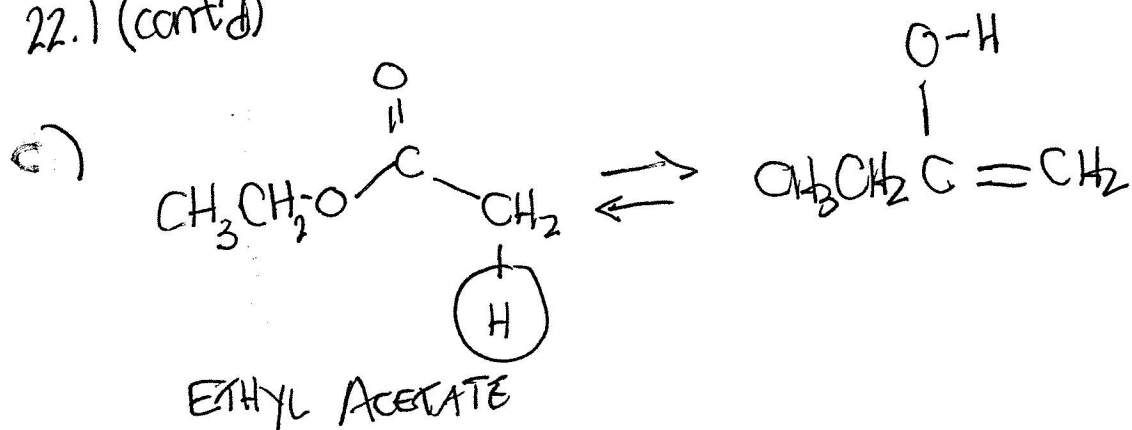
Any molecule that contains a protic functional group (alcohol, phenol, carboxylic acid) and an alkyl/aryl halide would have the same problem. Some additional examples are....



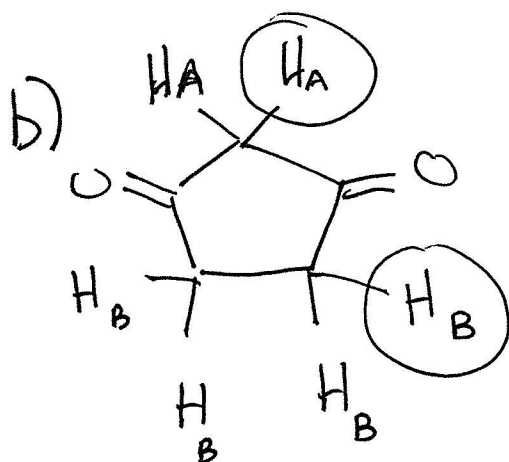
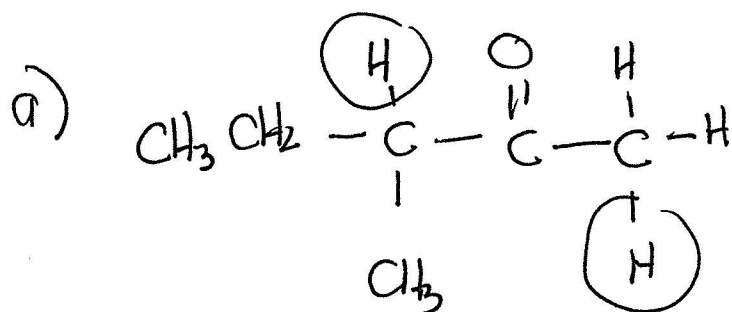
22.1



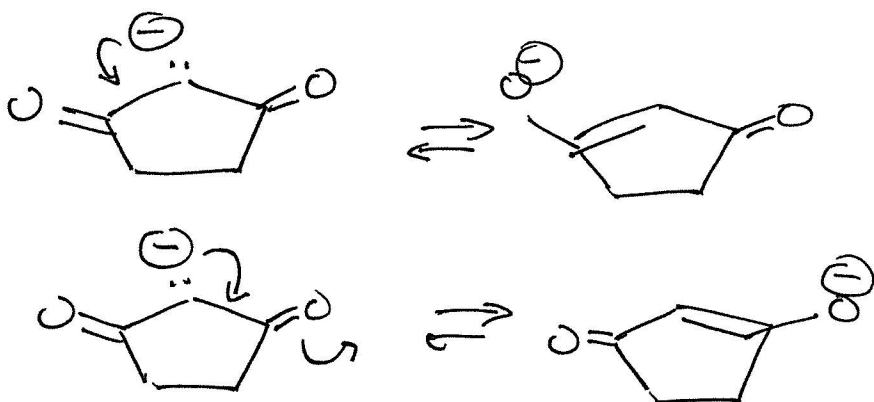
22.1 (cont'd)



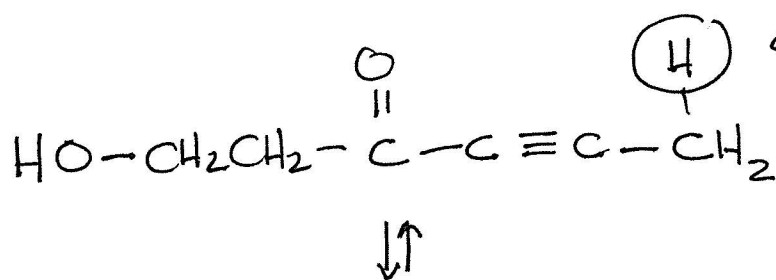
22.20 All α -hydrogens are acidic (CIRCLED)



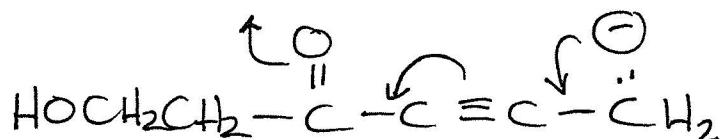
Both HA and HB are acidic but HA is MORE acidic b/c it has two carbonyl groups where the \ominus of the conjugate base can be delocalized.



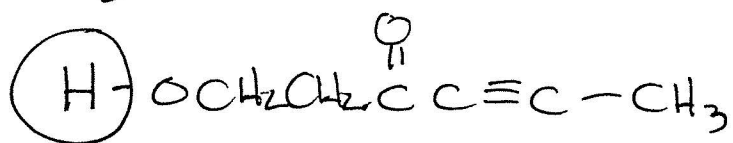
c)



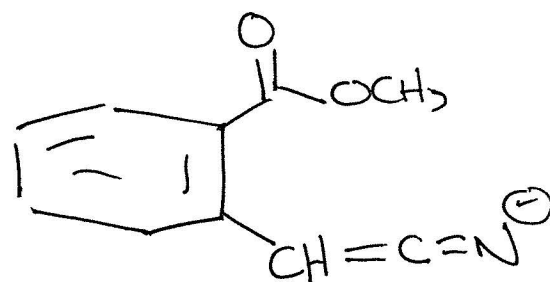
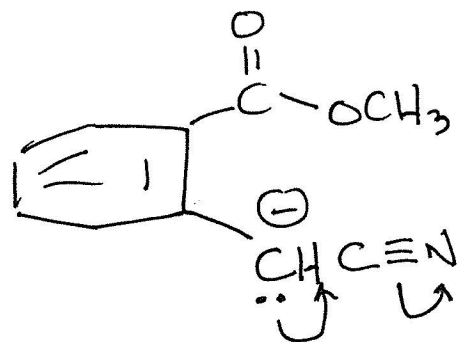
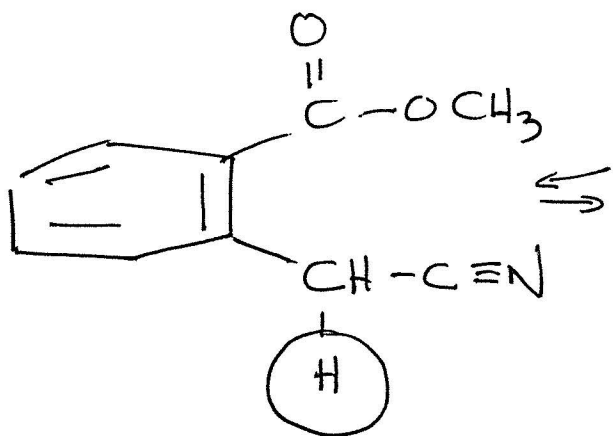
← Acidic b/c
resulting
conjugate base
is stabilized
through
resonance.



↙ alcoholic hydrogen weakly acidic



d)

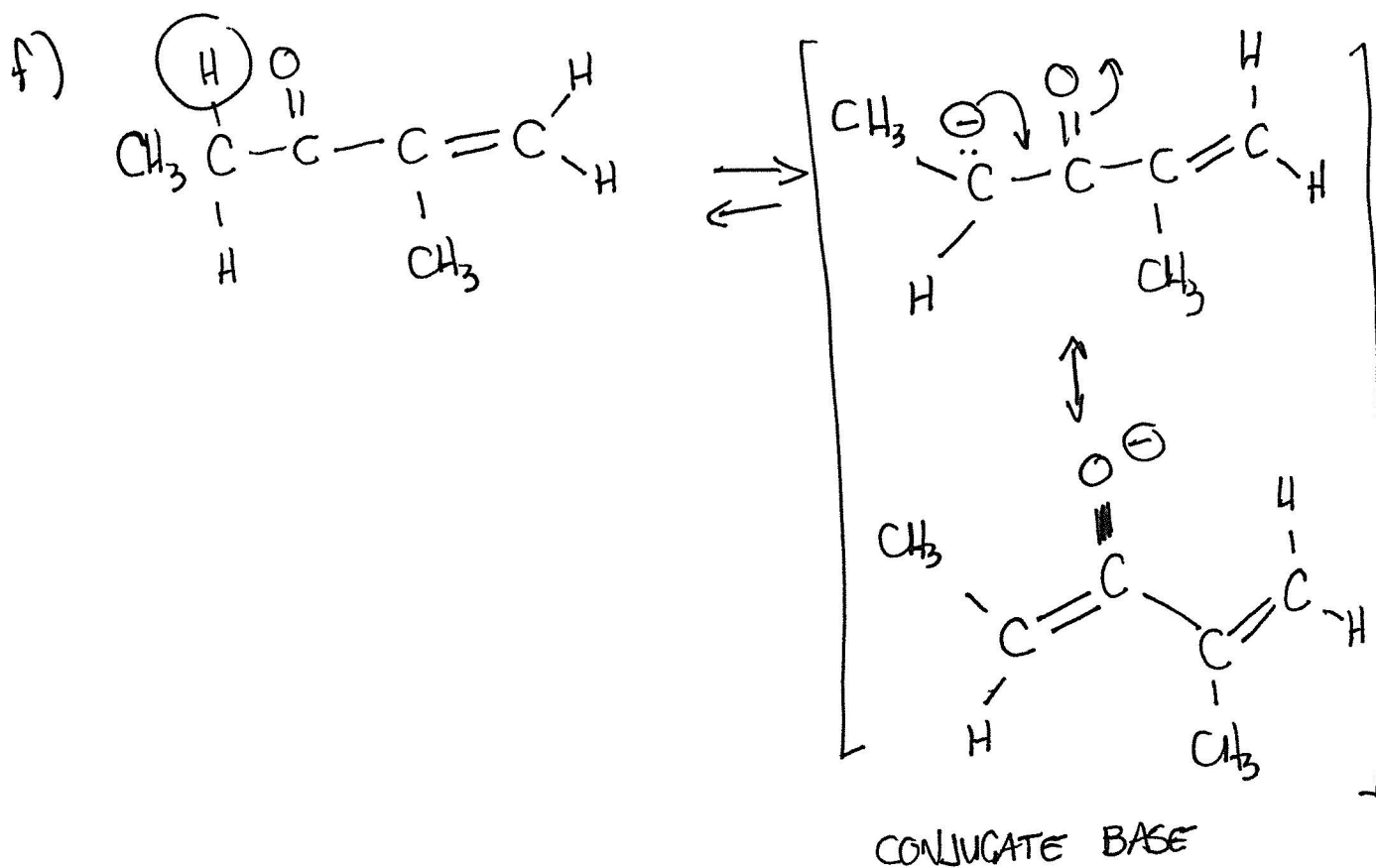
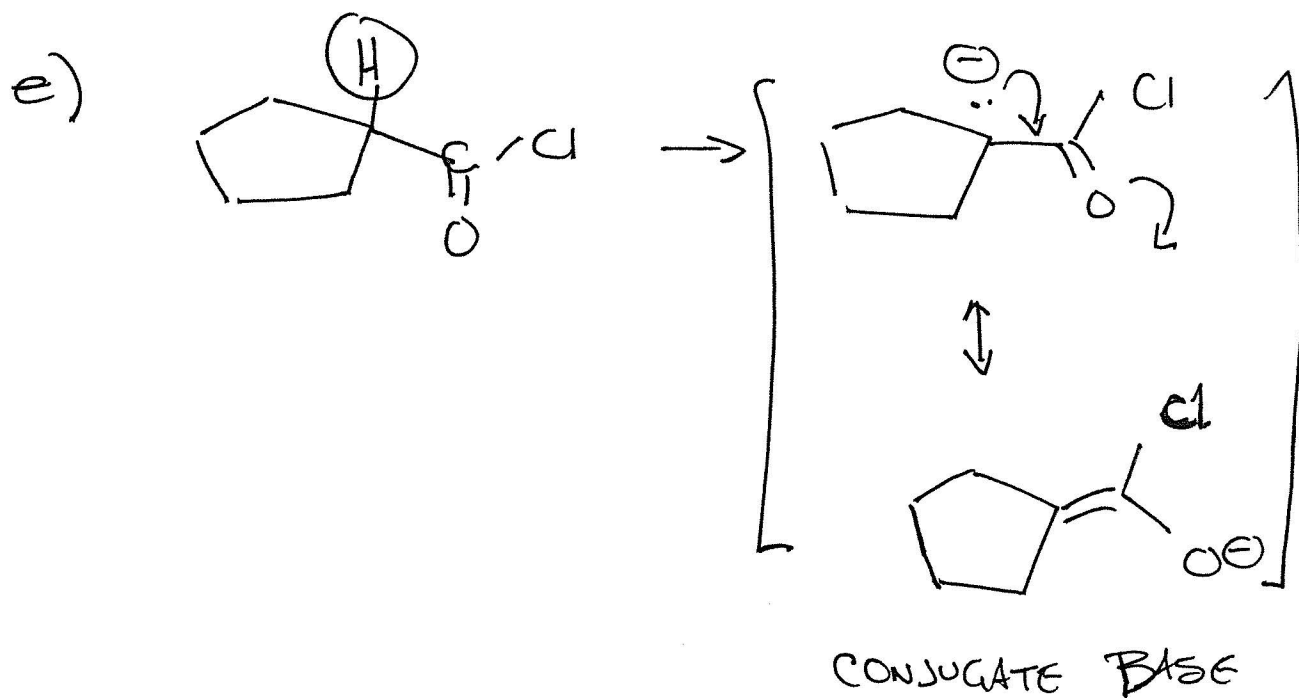


A hydrogen will be
acidic if its resulting
conjugate base is
RESONANCE stabilized.

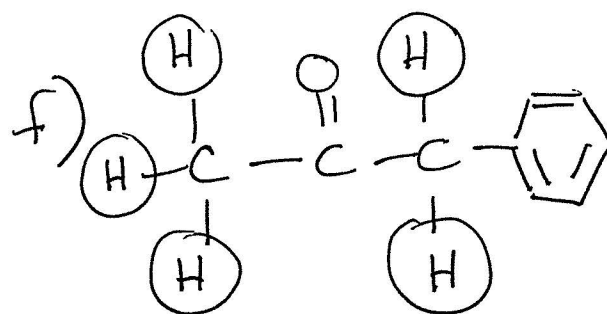
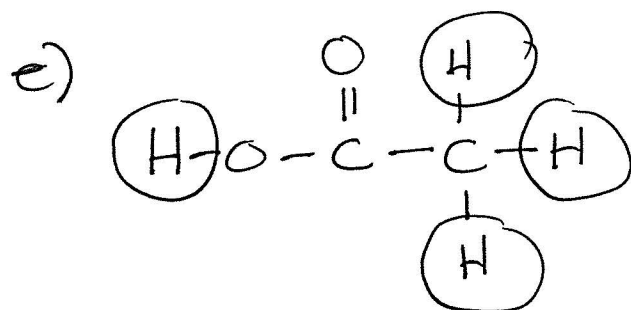
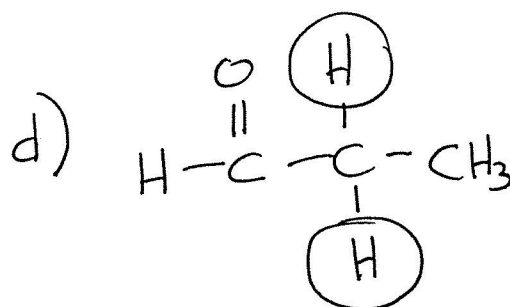
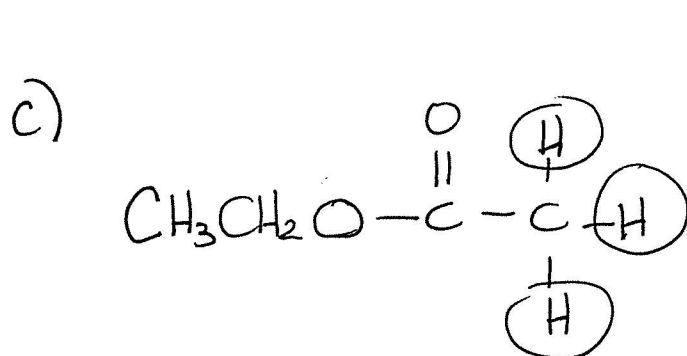
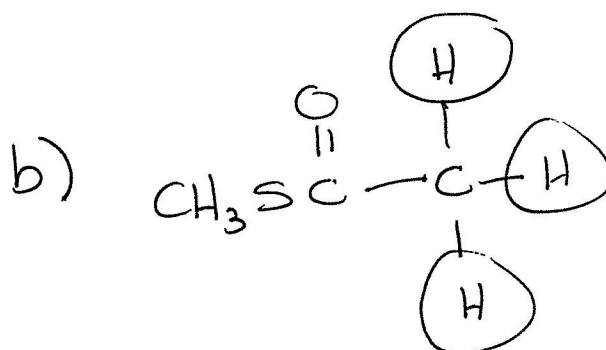
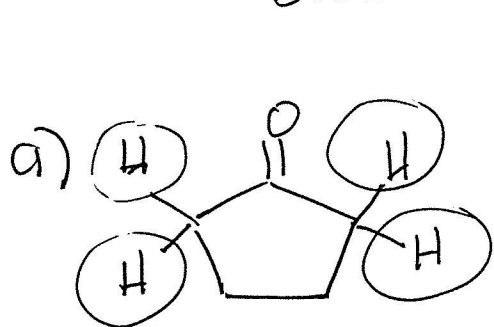
CONJUGATE BASE

22.20 (cont'd)

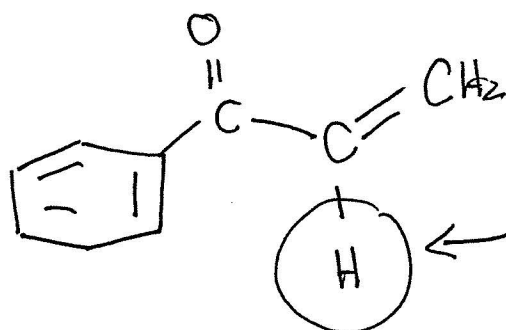
9-



22.2. α -H are acidic b/c the conjugate base is resonance stabilized.

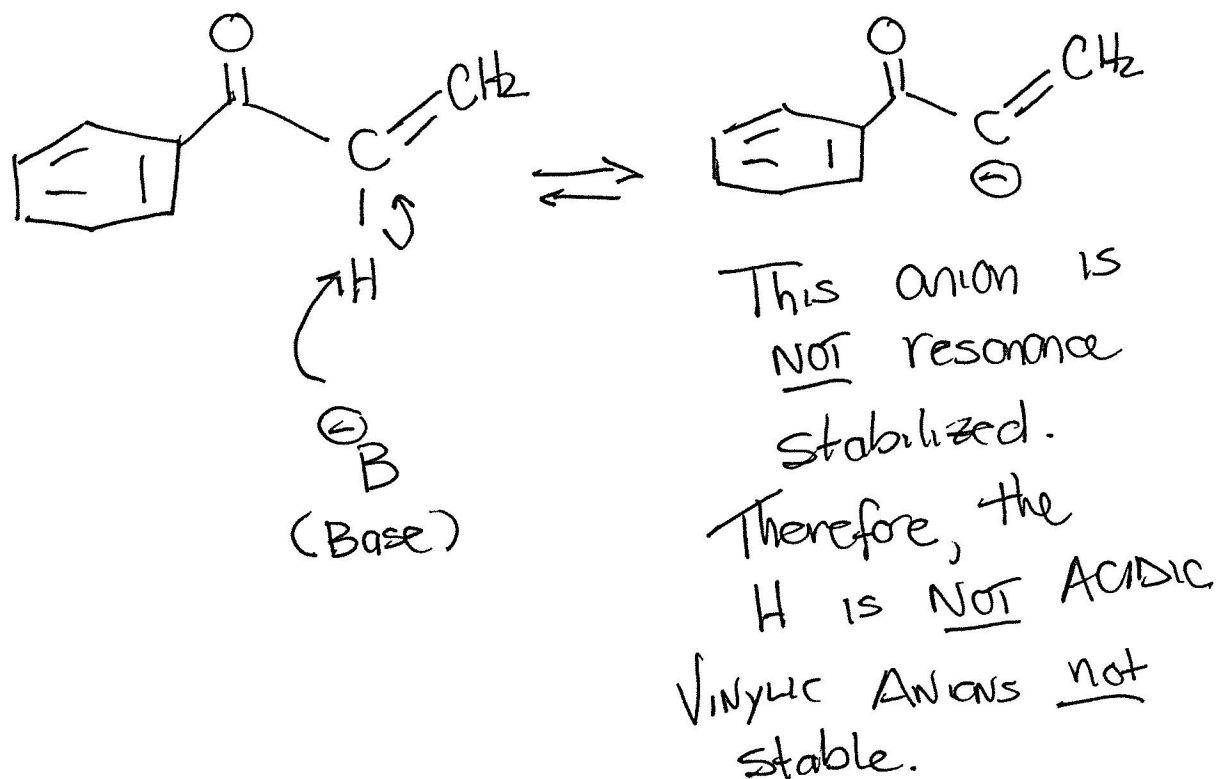


22.24

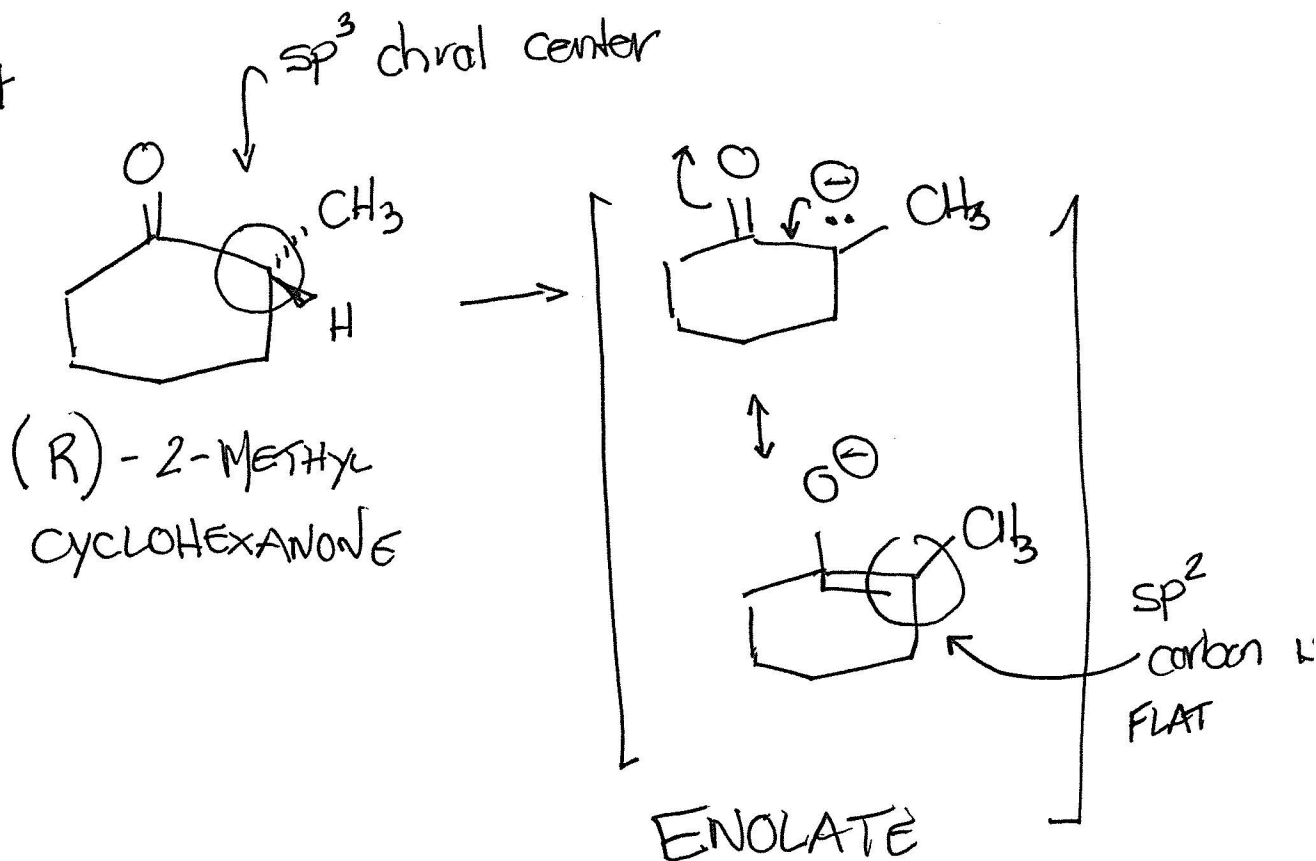


← This H is bonded to an sp^2 . The conjugate base that would be generated is a vinylic anion.

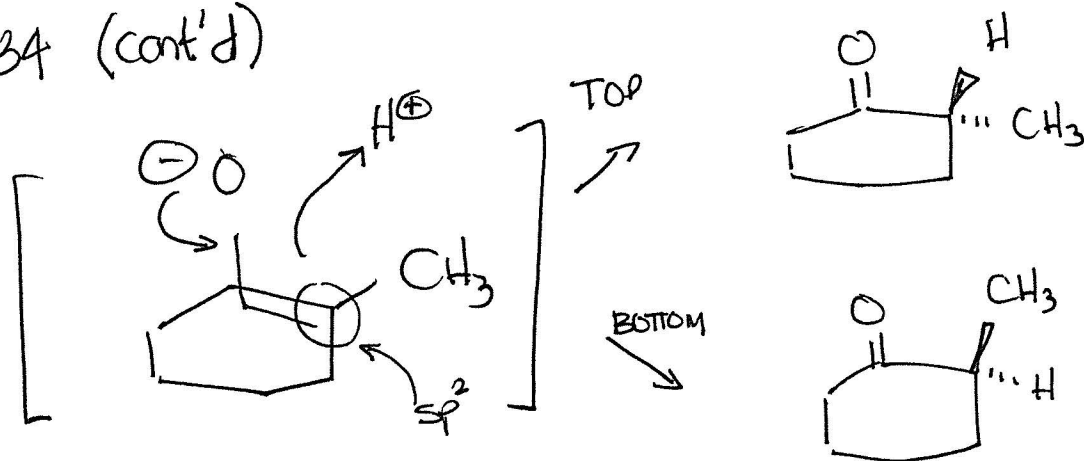
22.24



22.34



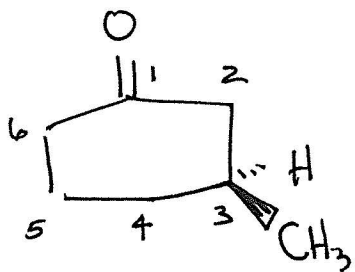
22.34 (cont'd)



When the sp^2 carbon of the enolate reverts back to the carbonyl, the H (H^+) reacts from TOP + BOTTOM of sp^2 carbon

RACEMIC mixture forms. 50:50 mixture of ENANTIOMERS.

22.35

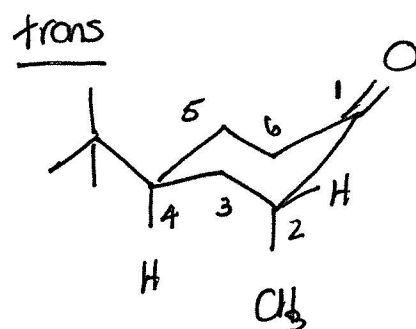
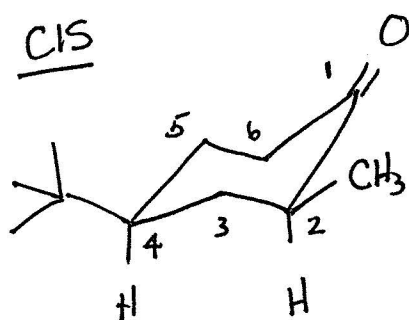
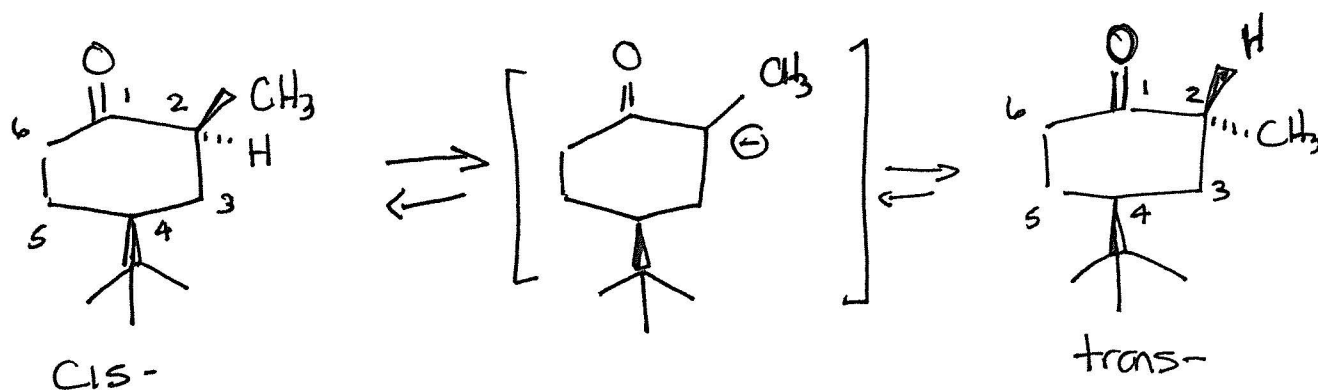


(S)-3-methyl-cyclohexanone

This compound does not racemize b/c the chiral center is NOT the α -carbon

The chiral center at C_3 is not affected by racemization.

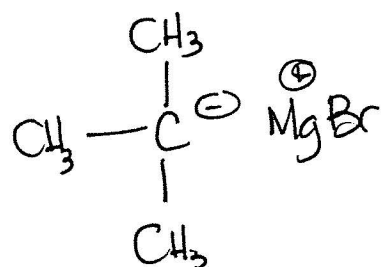
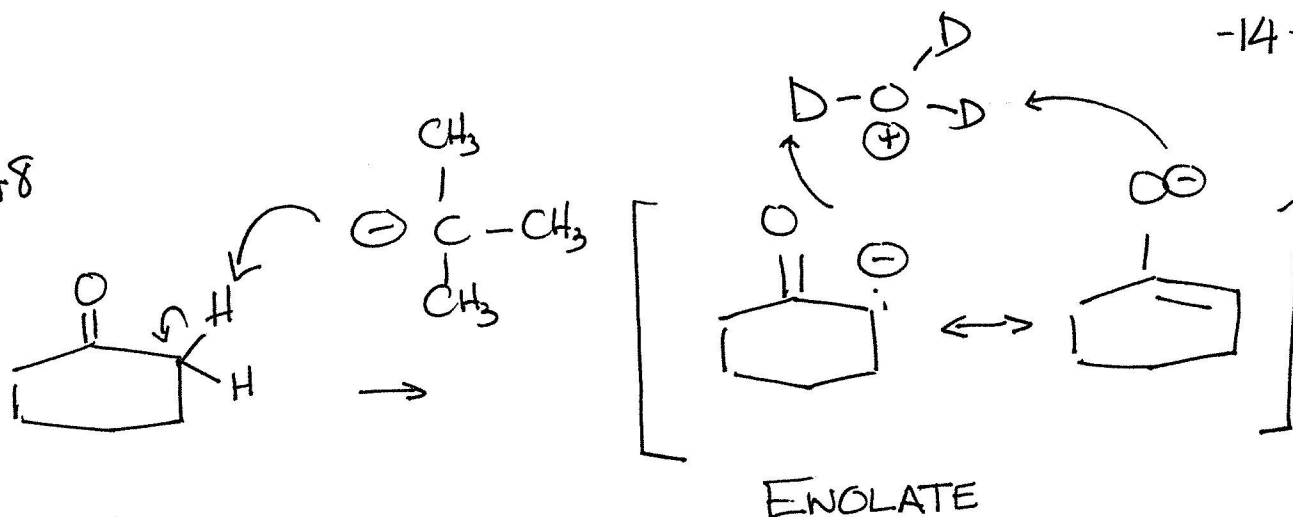
22.46



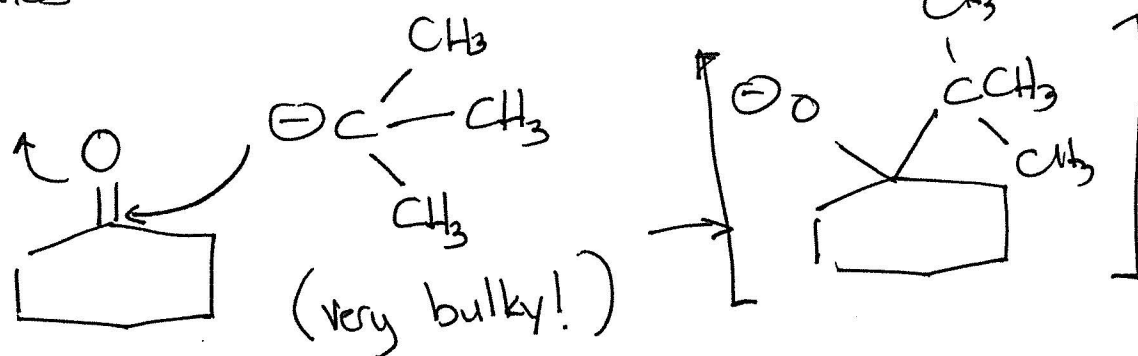
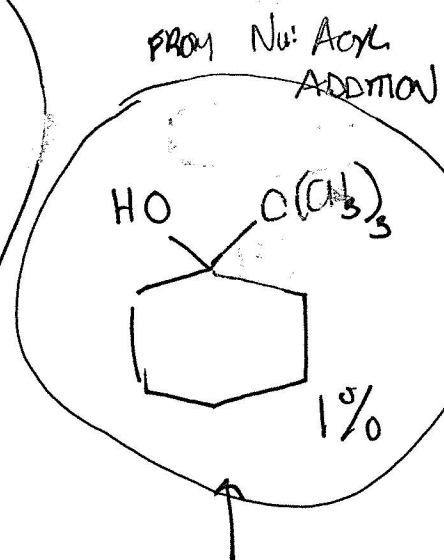
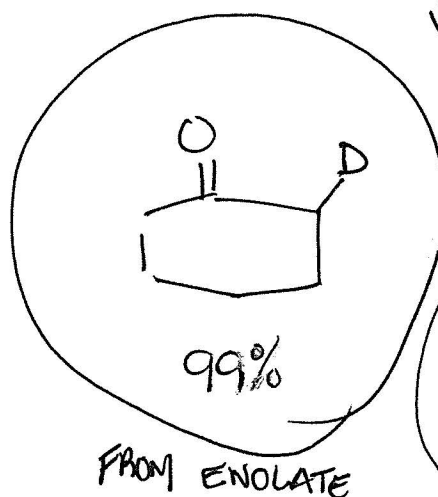
The cis-isomer has both substituents equatorial. With both substituents equatorial this isomer is MORE stable than the trans isomer, which has one substituent axial.

The trans-isomer has the t-Bu group equatorial and the methyl axial.

22.48



The tert-Bu Grignard reagent is too sterically bulky to react with the carbonyl. Instead, it behaves as a base and generates an enolate.



22.58

CARVONE

