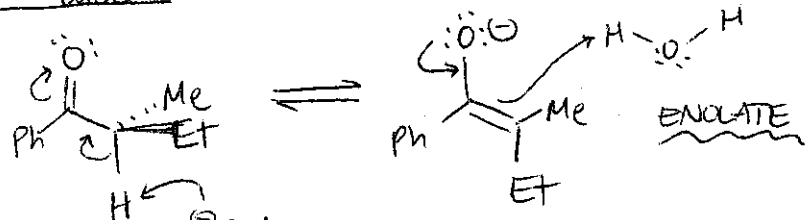
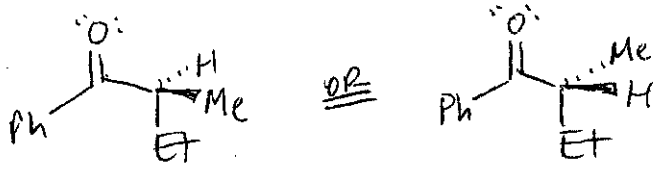
PROBLEM SET #9 SOLUTIONS CHEM 3231

1. In base:

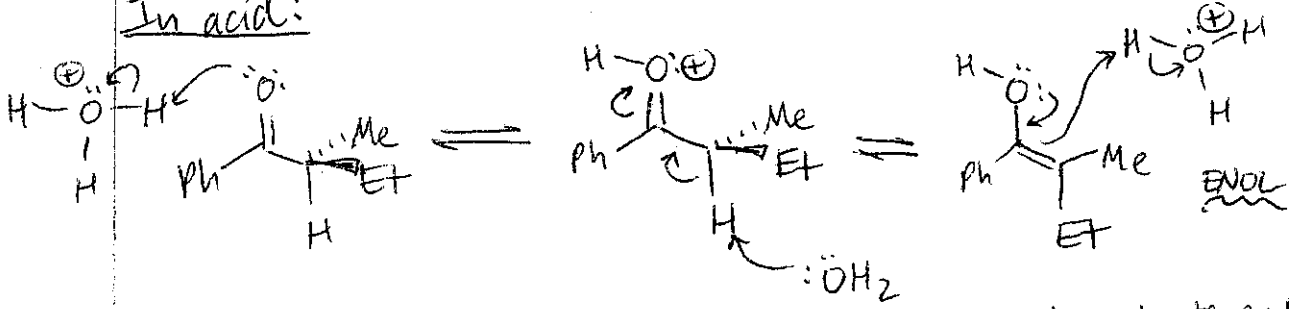


reprotonate enolate from top or bottom

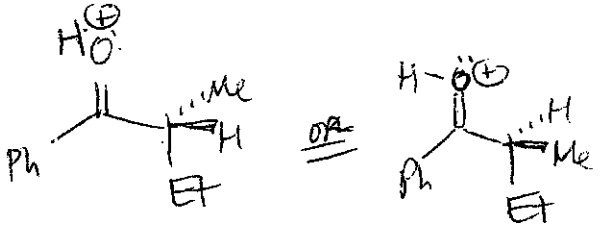


Ⓐ because the enolate (which is flat) can be reprotonated from the top (OR) the bottom, so get racemic mixture

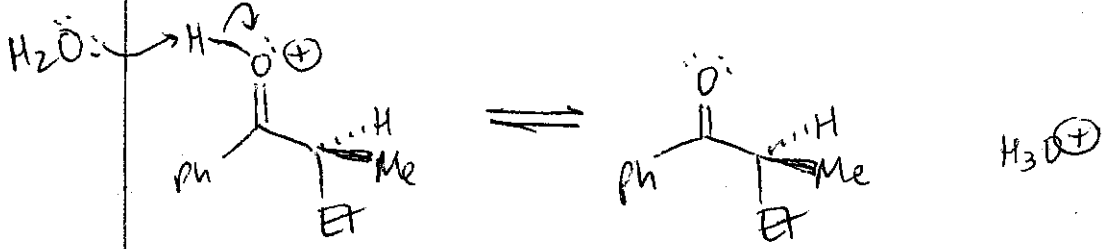
In acid:



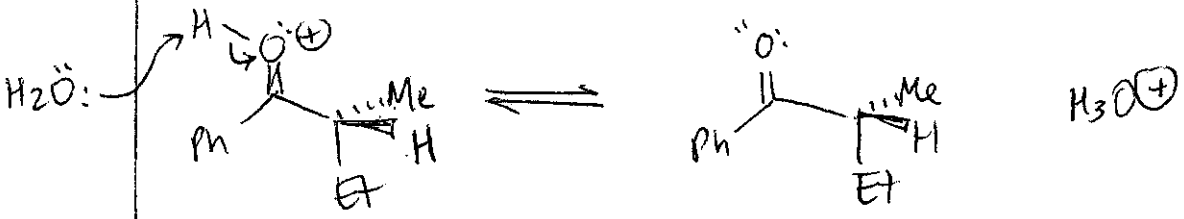
reprotonate enol from top or bottom



(OVER)

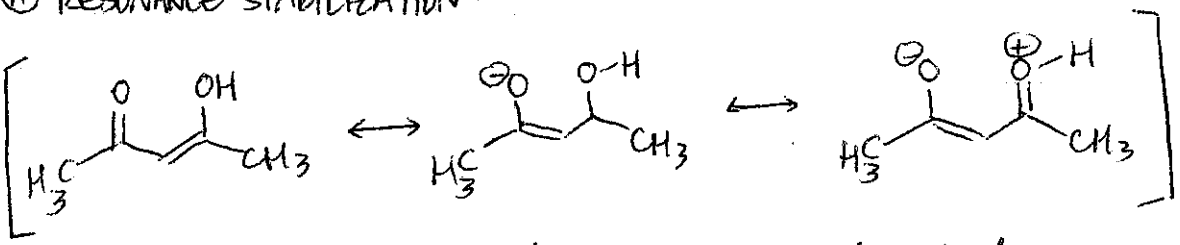


AND



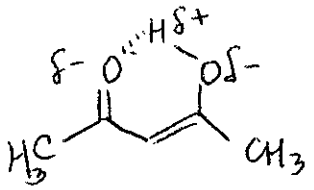
2. The enol is stabilized by a couple of things:

(A) RESONANCE STABILIZATION:

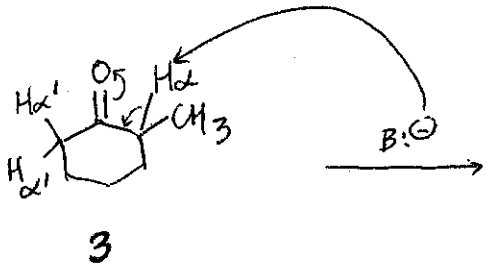


carbonyl and C=C are conjugated

(B) INTRAMOLECULAR HYDROGEN-BONDING:

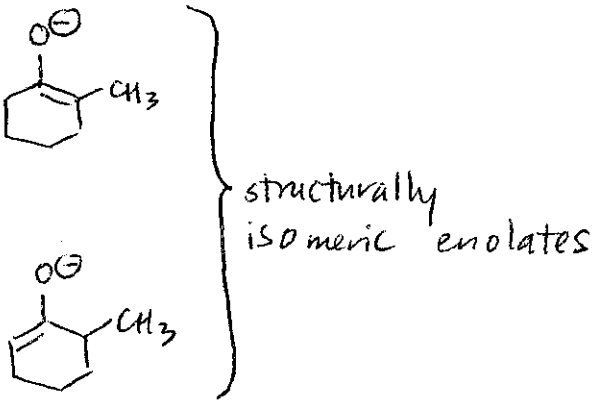


3.

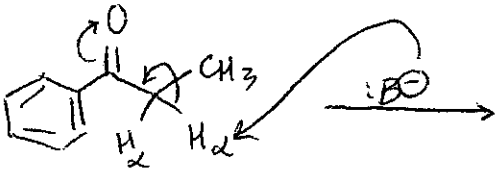


3

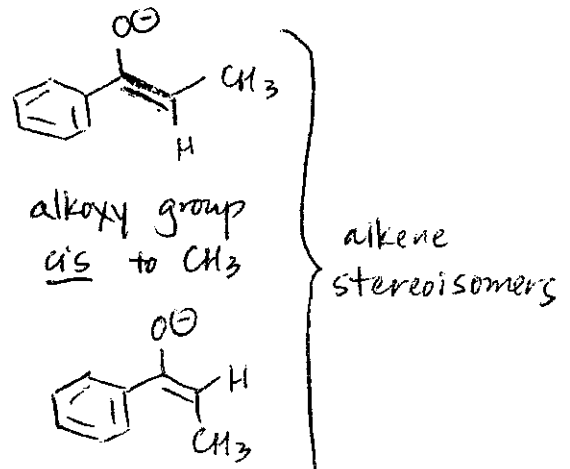
(OR) remove $H_{\alpha'}$



structurally isomeric enolates



4



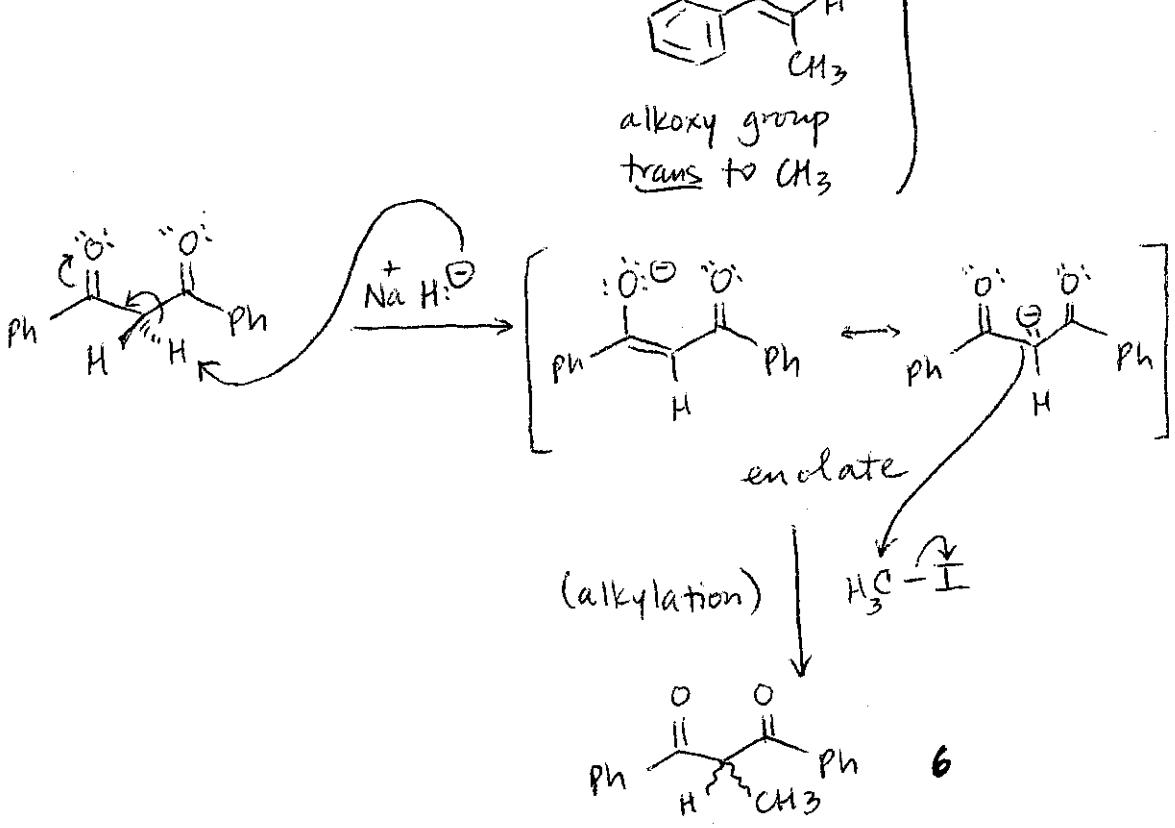
alkoxy group cis to CH_3

(OR)

alkoxy group trans to CH_3

alkene stereoisomers

4.

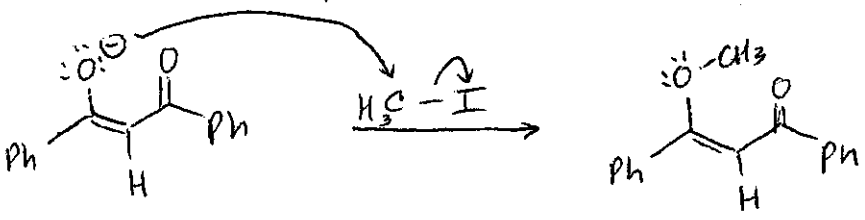


enolate

(alkylation)

6

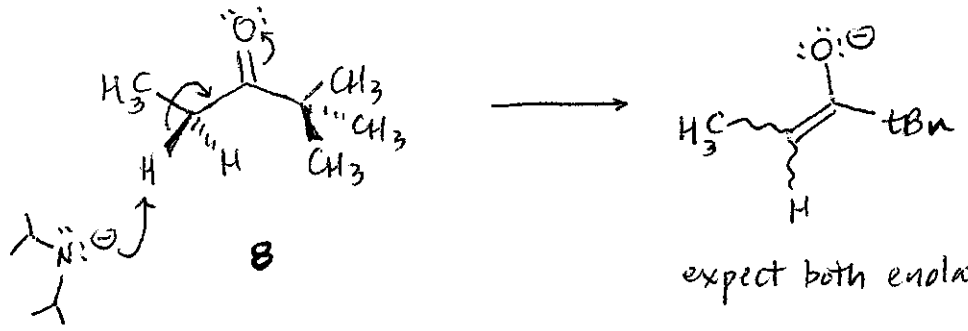
5. From the enolate of #4:



7

alkylation can occur at oxygen

6.

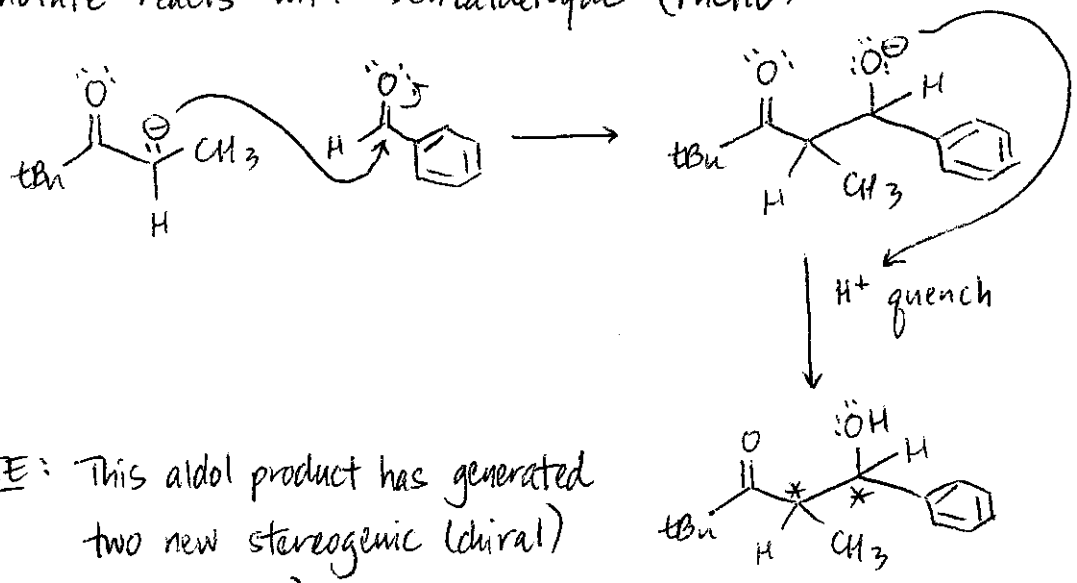


8

expect both enolate isomers

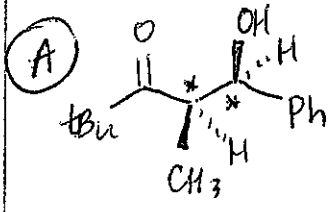
enolate can form to only one side of carbonyl

Enolate reacts with benzaldehyde (PhCHO):

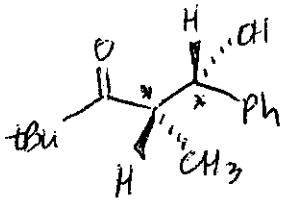


NOTE: This aldol product has generated two new stereogenic (chiral) centers (*).

With two chiral centers, there are 4 (2^2 stereoisomers) possible stereoisomeric products in 2 pairs of enantiomers.



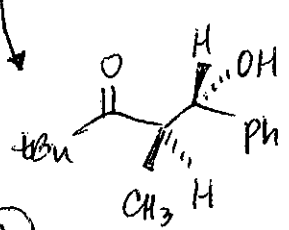
R, R



S, S

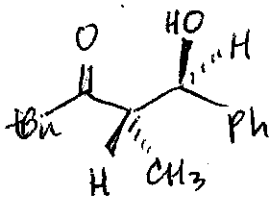
B] enantiomers (identical ^1H, ^{13}C NMR's)

stereomers
fferent spectra)



C

R, S

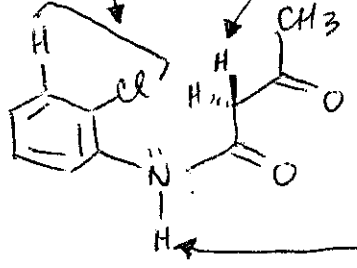


D

S, R

D] enantiomers (same spectra)

7. The key is to recognize that amide ($:\overset{\ominus}{N}H_2$) is a very strong base — look at possible reaction sites on **9**:

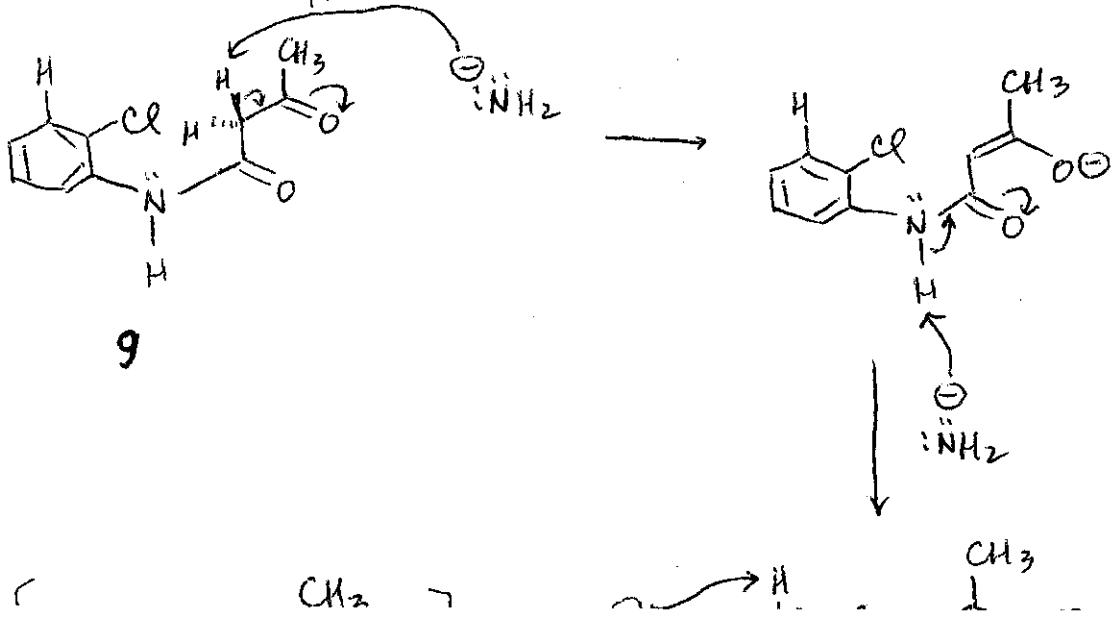


fairly acidic (α to <u>two</u> carbonyls)

fairly acidic (α to carbonyl <u>AND</u> on nitrogen)

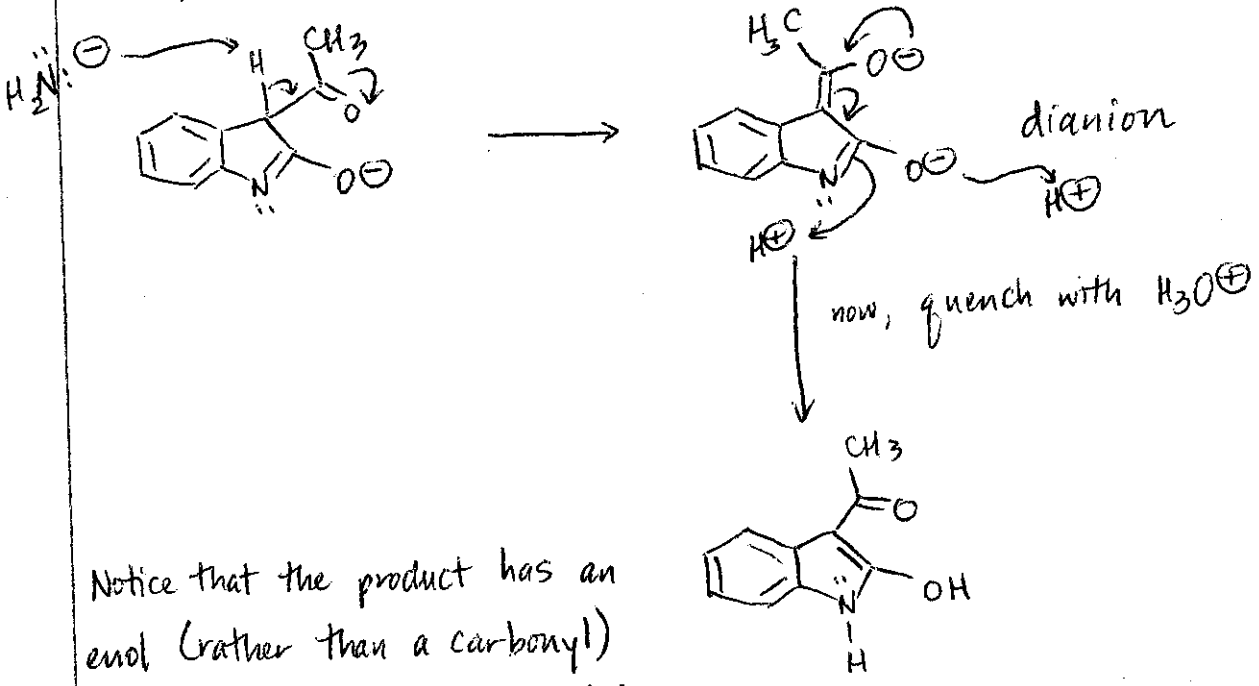
can form benzyne by elimination of HCl

Mechanism — precise sequence of deprotonations could be different :



9

Under the very basic rxn conditions, this molecule is in the form of its dianion:



Notice that the product has an enol (rather than a carbonyl) in the 5-membered, N-containing ring ... because the pyrrole unit,

is aromatic!