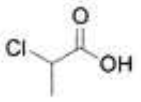
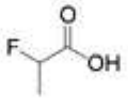
CHEM 3331 **Third Hour Exam** **Summer 2005**
July 28, 2005

Name: Key

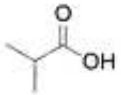
1a) Which of the following carboxylic acids is the most acidic, and which is the least acidic? Explain your answers (this is necessary for full credit). (6 pts)



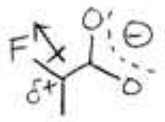
A



B



C



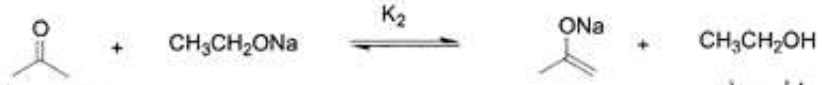
(See answer)

Most acidic: B +1 Least acidic: C +2

F is inductively e⁻ withdrawing and places δ+ on the α C, +2 stabilizing the delocalized ⊖ in the conjugate base. F is more +1 EN than Cl, so this effect is more pronounced in B than A; and C does not experience this stabilization.

1b) Which of the following equilibria favors *products* more? Circle it, and explain your answer (this is necessary for full credit). (6 pts)

pka 18-20 pka 36 +3



pka 18-20 pka 16

$K_1 \approx 10^{18}$ while $K_2 \approx 10^{-2}$ (ballpark numbers). +3
Equilibrium position favors the weaker acid/base pair — products in the K_1 equilibrium are much weaker acid/base than reactants.

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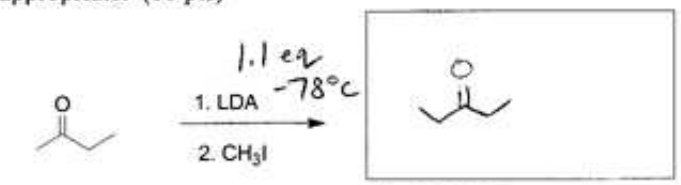
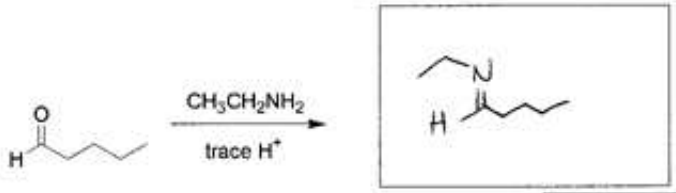
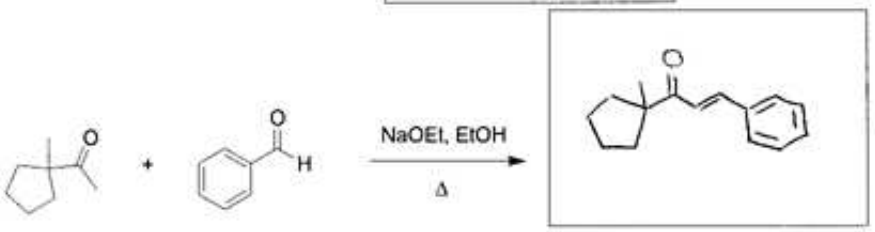
2a) Predict the products of the following reactions. Show stereochemistry where appropriate. (18 pts)



kinetic enolate formation and alkylation

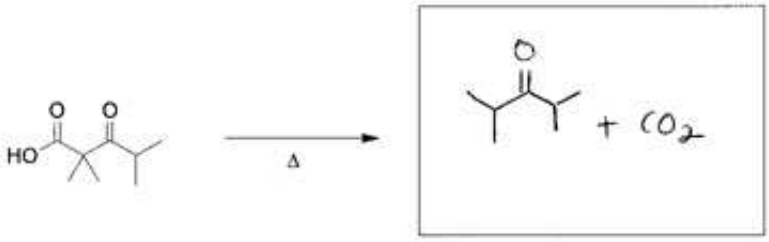


imine formation

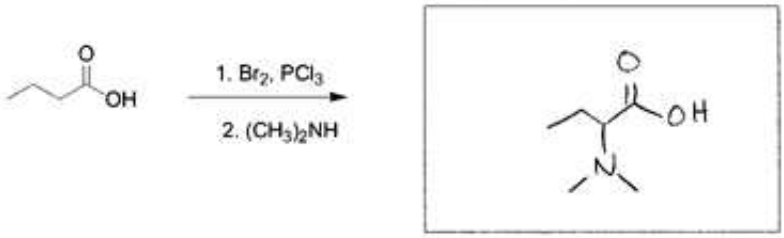


aldol condensation

Baeyer Villiger [O] Retention of stereochemistry



Decarboxylation of a β-keto acid



Hell-Vollhard-Zelinsky followed by an S_N2 reaction to displace Br

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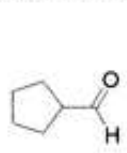
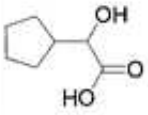
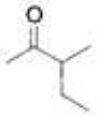
2b) Provide the reagents necessary to carry out the following transformations. Some transformations may require more than one step (18 pts).



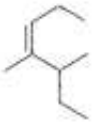
1. $NaCN$, $H^{\oplus}$
2. $H_3O^{\oplus}$



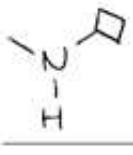
1. cyanohydrin formation
2. hydrolysis

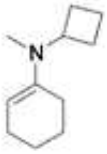


$Ph_3\overset{\oplus}{P}-\overset{\ominus}{C}HCH_2CH_3$



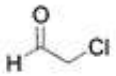
Wittig



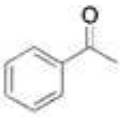


enamine formation

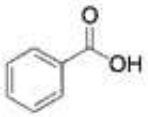
Cl_2
$H^{\oplus}$



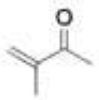
$H^{\oplus}$-catalyzed α halogenation



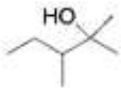
(3 eq) (4 eq)
Br_2, $HO^{\ominus}$
then $H_3O^{\oplus}$



haloform reaction



1) Me_2CuLi, then $H_3O^{\oplus}$
2) MeMgBr or MeLi then $H_3O^{\oplus}$



1,4 addition of cuprate, then 1,2 addition of methyl Grignard or organolithium

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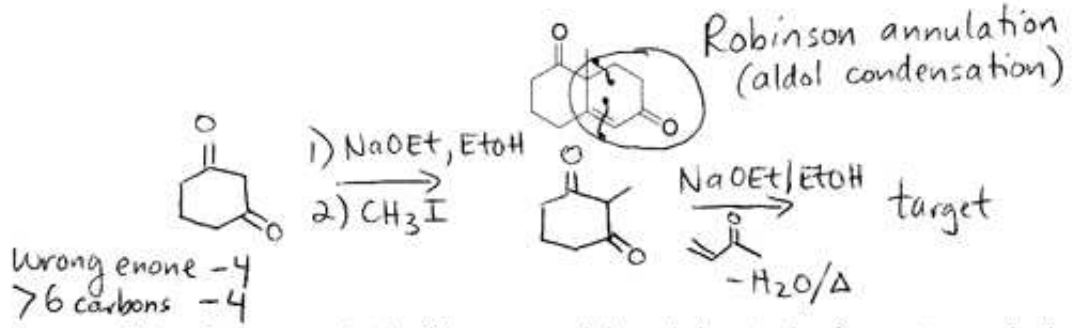
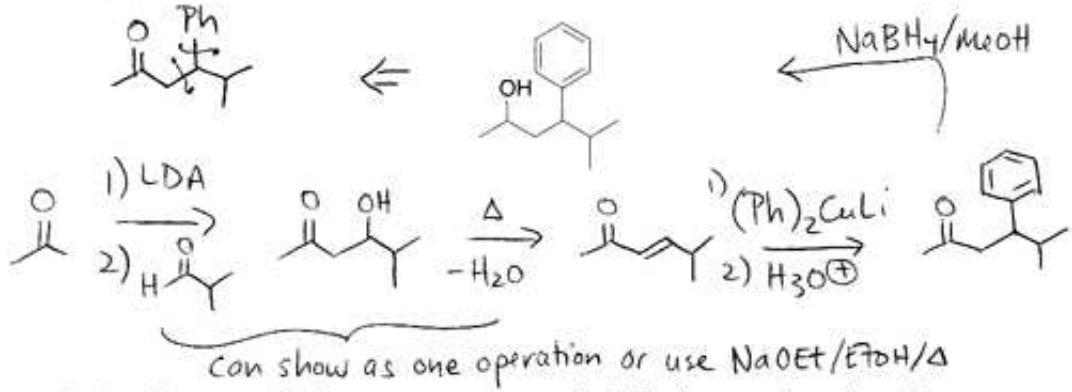
3a) The Wieland-Mischler ketone is a common precursor to the synthesis of steroids. Design a synthesis for this ketone using starting materials that contain 6 carbons or less, and any inorganic reagents (8 pts).

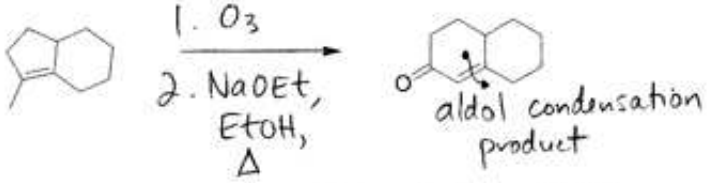


wrong enone -4
>6 carbons -4

3b) Design a synthesis of the compound shown below starting from acetone and using organic reagents of 6 carbons or less, and any inorganic reagents (9 pts).



3c) Show a synthetic sequence to carry out the following transformation. You may use organic reagents containing 3 or fewer carbons, and any inorganic reagents (6 pts).



Or dihydroxylation (OsO_4) then HIO_4
followed by NaOEt, EtOH, Δ

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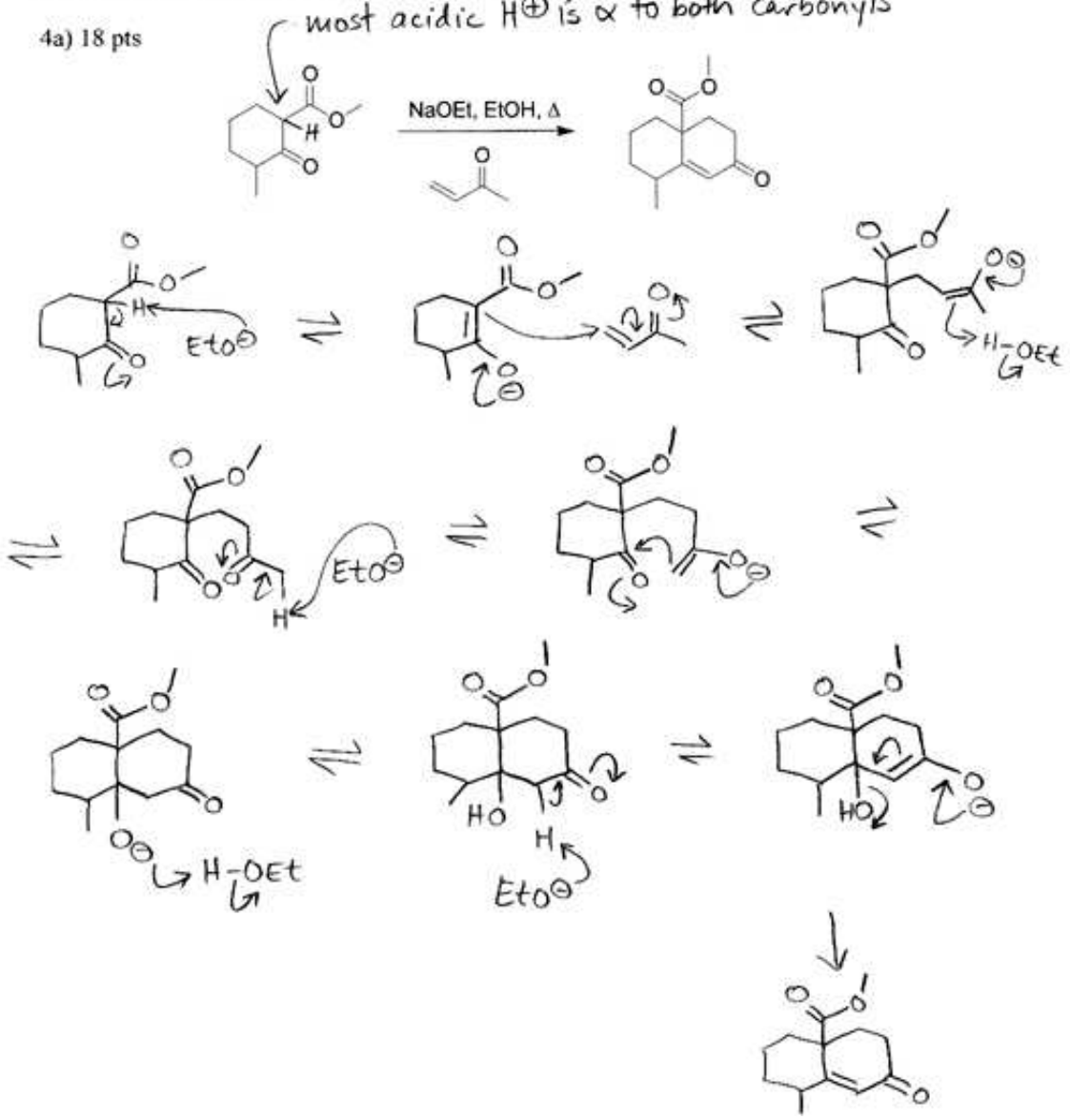
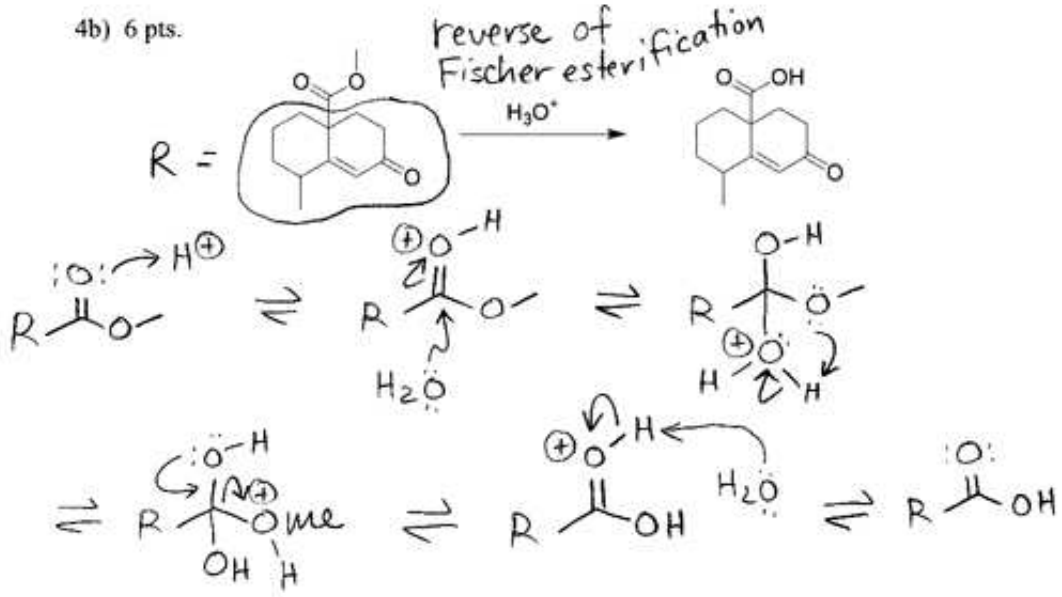
4) Draw an arrow-pushing mechanism for each of the following transformations. Show all necessary lone pairs, formal charges and arrows.

4a) 18 pts



4b) 6 pts.



4c) 5 pts.