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OFFICE HOUR CHANGE NEXT WEEK:
MONDAY AFTER CLASS, NOT WEDNESDAY

FINISHED WITH CHAPTER 21 ("CARBOXYLIC ACID DERIVATIVES") (C.A.D.)

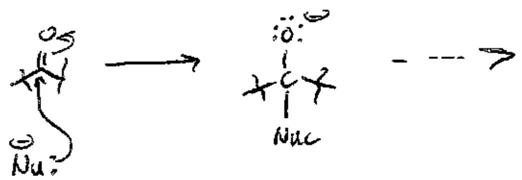
→ READ SECTION 21.11 CAREFULLY

LIST OF PREVIOUSLY STUDIED RXNS FOR SYNTHESIS OF C.A.D. (FLASH CARDS)

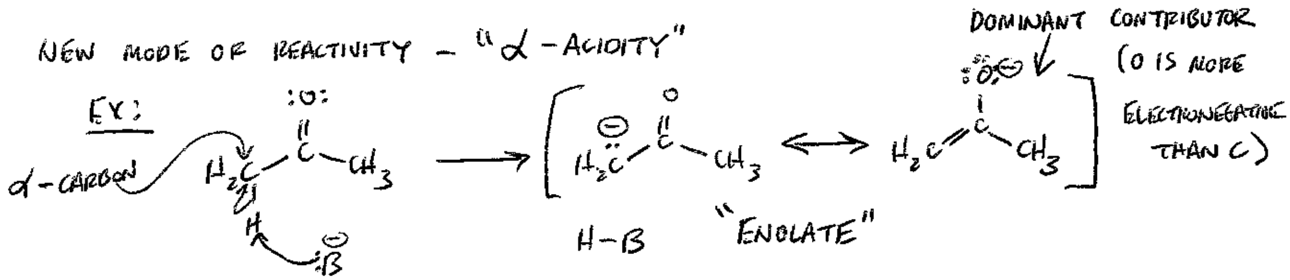
CHAPTER 22 - ENOLATES & ENOLS

REC. PROBLEMS: 1-9, 11-30, 33, 34, 36, 37, 39-89

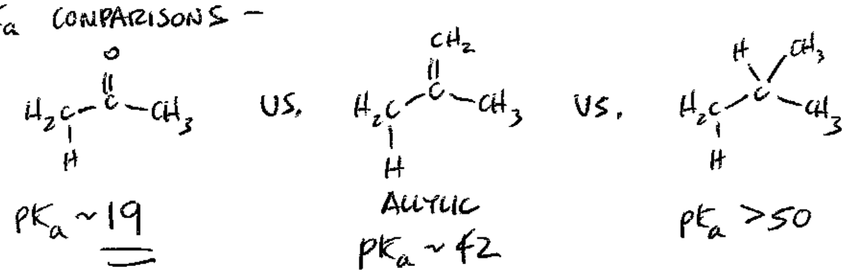
PERSPECTIVE: REACTIVITY PATTERNS



NEW MODE OF REACTIVITY - "α-ACIDITY"



pKa COMPARISONS -



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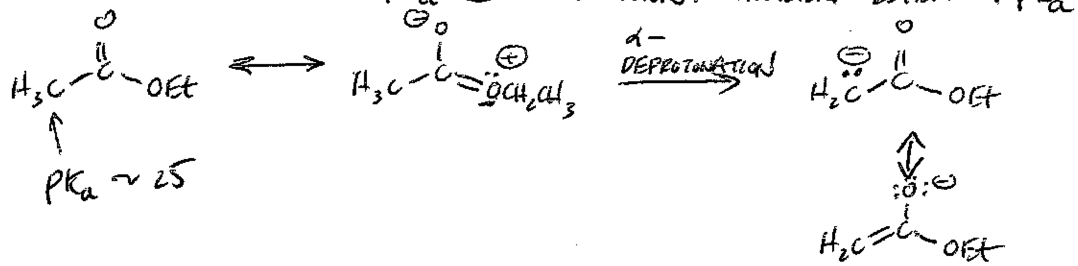
TYPE OF CARBONYL INFLUENCES pK_a @ α-POSITION. CONSIDER ESTER α pK_a

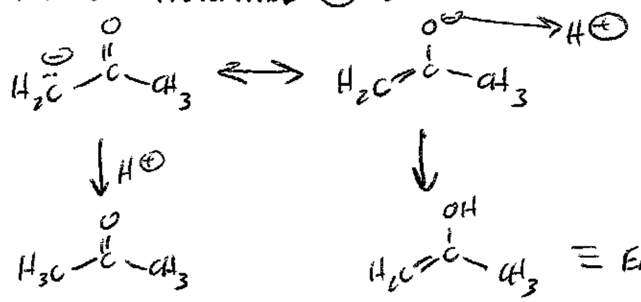


WHY HIGHER pK_a (i.e., LOWER ACIDITY) @ α-CARBON FOR ESTER RELATIVE TO ALDEHYDE/KETONE?

LOSS OF RESONANCE PRESENT IN CONJUGATE ACID FORM OF ESTER

→ BUT, NO RESONANCE IN ALDEHYDE OR KETONE

ENOLATE CAN BE PROTONATED @ 2 SITES



ENOLS ARE USUALLY MUCH LESS STABLE THAN CARBONYL ISOMERS

• CARBONYL & ENOL FORMS INTERCONVERT RAPIDLY IF ANY ACID OR BASE CATALYST PRESENT.

• EXAMPLES OF CARBONYL ⇌ ENOL EQUILIBRIUM

TYPICAL ALDEHYDE/KETONE

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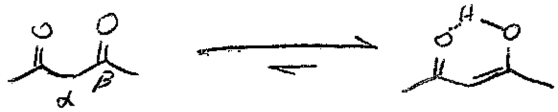
THUS, RXNS CAN PROCEED VIA ALDEHYDE / KETONE ENOL, BUT NOT VIA ESTER ENOL

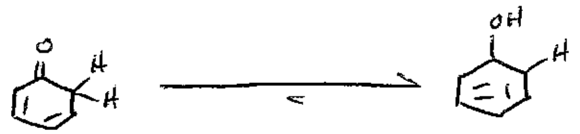
(1) β - DICARBONYL



k_{eq}: 10 – 100

NOTE: • H-BOND (6-MEMBERED RING)
• CONJUGATION

(2) PHENOLS



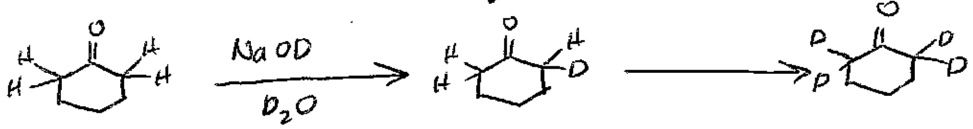
k_{eq}: 10^{14}

NOT AROMATIC → AROMATIC

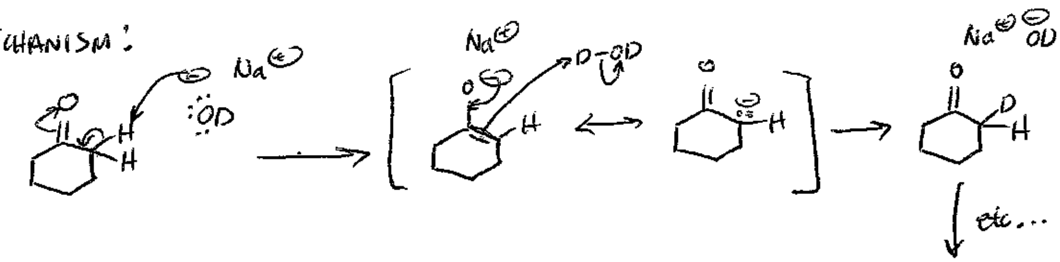
REACTIONS INVOLVING α - ACIDITY OF CARBONYL COMPOUNDS

(1) H/D EXCHANGE (D = DEUTERIUM)

ALKALINE CONDITIONS (BASE - CATALYZED)



MECHANISM:



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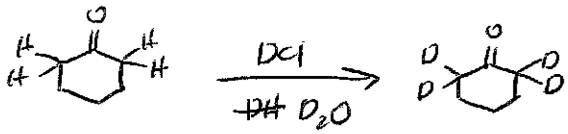
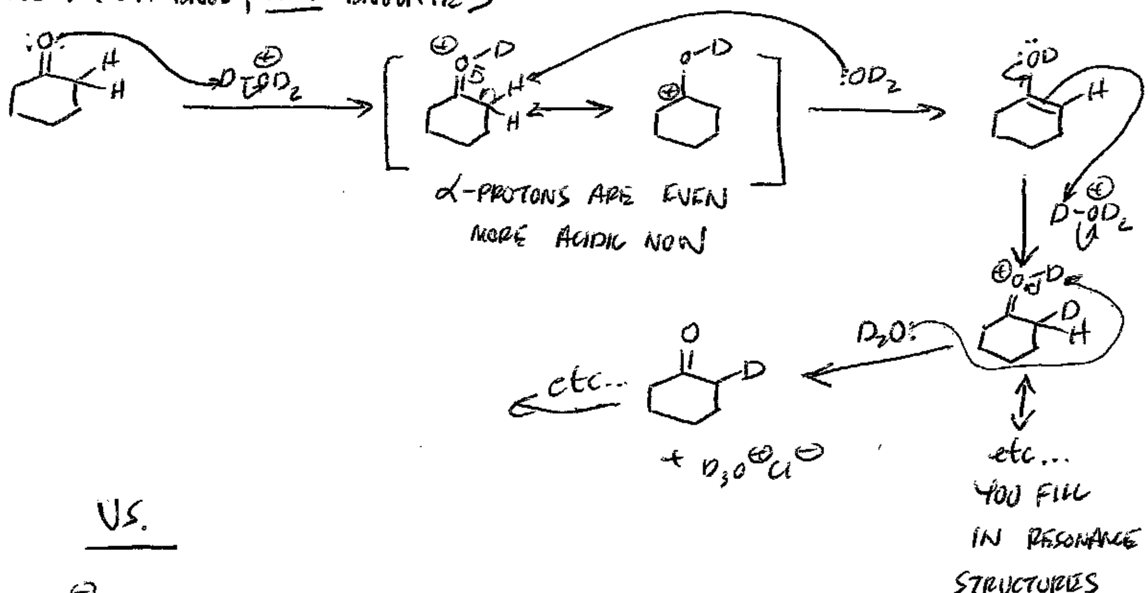
ACIDIC CONDITIONS (ACID CATALYSIS)



MECHANISM (VIA ENOL, NOT ENOLATE)



VS.