***Supplement 10: NEW REACTIONS OF KETONES & ALDEHYDES***

*CHEMISTRY 4524 ORGANIC CHEMISTRY II Spring 2016*

**Overview**

**I II2 III IV**

**4 reaction classes1:oxidations of...** **carbonyl reductions to...** **additions of** **base-driven α-H reactions (α subst. and condens.)**

*-****aldehydes to acid******-to alkenes(Wittig)*** *-1,2o amines ---->immines,ennamines -* ***Cannizzaro (no α-H) => self oxid/red***

*-****ketones cleaved*** *-*  ***CN---> difunctionals*** *-****Condensations (w/ α-H) => difunctionals (e.g. aldol)***

***(Baeyer-Villiger)*** *- ROH--->acetals, ketals -****halogenation at α-H=> difunctional carbonyl halide***  *-****haloform & perioidate rxn******-NaC≡C or BrMgC≡C🡪alknyl alcohol***

*1the acyl substitutions have been covered 2=acyl addition*

*With* ***addition)***

**Details & Notes**

**I.** Oxidations (R=aliphatic or aromatic) Notes

KMnO4 or K2Cr2O7 or Ag­­2O/NH3

**1)** RCHO--------------->RCOOH -aldehydes make acids....easy to run, since no net cleavage

-KMnO4 > K2 Cr2 O7 > Ag2O in NH3 (Tollen’s)

C HO🡪COOH & CHO-🡪 COOH & won’t convert xylene to acid

O **O**R’ O xylene-->HOOC-Ar-COOH xylene-->CH3-Ar-COOH silver mirror reaction

R || | ||

**2)** C=O + R” C-**O**-OH-------> RC=O + R”C-OH -Baeyer-Villiger oxidation...inserts O into ketone to make ester at larger of R or R’

R’ (peroxy-acid) a useful way to insert an O to make esters of a ketone

NaOI

3) CH3C=O -------------------> CH3I + Na+ O-C=O -ketones cleave, but keep C=O intact...harder to run because of C-C cleavage

| ***(haloform test)***  | -Haloform test is positive if yellow CH3I forms=> methyl ketone ID (not in text)

R R

4) HIO4 /KMnO4 (cat)

R’C=O ----------------> R’COOH + RCOOH -Periodate test is like ozonolysis (not in text)

| ***(periodate test)***

R

**II.** Reductions (R=aliphatic or aromatic) Notes

**A** dmso

**5)** RR**’C**=O + Ar3 P=C-----------> RR’**C**=C***AB*** -***Wittig reaction*** : a ***general route to alkenes***

***an ylide B phosphine alkyl halide*** in benzene `ylide’

to make ylides: Ar3P: + Cl-CH***AB -----> Ar3P=***C***AB*** +HCl

**6)**

**III.** Additions (R=aliphatic or aromatic)

**C**N- H+ -**attacks starts at carbonyl C by CN-** , **a nucleophile**

6a) RCHO ------> RC**-CN --->**RCH**-COOH -**a difunctional hydroxyl acid

| | -further dehydration produces C=C-COOH product

OH OH -industrially significant...nitriles, starter for polymers

-CN- is dangerous !!!

R’ R’ R’

|  **CN-** | H+ |

6b) R-C=O ----> R-C**-CN**----------> RC-**COOH**

| |

OH OH OH

**[cyanohydrin reaction] |**

**6c) either cyanohydrin above + LiAlH4/ then H2O 🡪 RR’C-C-NH2 -Reduction of CN to C-NH2**

OH

***H2O/H+ |***

***7) >C=O + BrMgC≡CH or Na+C≡CH- -----🡪 >C-C≡CH + Mg(OH)Br or NaOH difunctional alkynl alcohol***

**8) amine addition (586-587)**

Primary amines yields imines (C=N) with 0 and primary amines) and don’t involve carbonyl alpha H

NH3 + >C=O 🡪 >C=NH +H2O

RNH2 + >C=O 🡪 >C=NR + H2O

Secondary amines yields enamines (C=C-NRR’) and involves alpha H of carbonyl

**H**

RR’NH +

-CH -C=O 🡪 -CH=C-NRR’ + **H-**O-H

| |

R” R”

**IV.** α-H and base-driven condensation reactions Notes α-H condensation ref. see below

9) >C(O)-CRR’-H + X2 –--acetic acid---> >CO-CRR’-X -route to difunctionals (ex: Ar-C(O)-CHCl-CH3---------> Ar-C(O)-CH=CH2)

***(α-H site halogenation)*** KOH

NaOH**more reduced more oxidized****-view as self-oxidation/reduction**

10)2HCHO------------>CH3OH + HCOOH -base driven, no α-H. A bit `odd’ (no carbanion)...but still nucleophilic attack

***(Cannizzaro reaction)* -**can mix HCHO and ArCHO for crossed Cannizzaro (3 possible alcohols)

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BrBr Br OH

| | | |

11) RCH2COOH + PBr3/ Br2🡪 RCH-C=O then H2O🡪 CH3CH-C=O Hell-Volhard-Zellinsky Reaction (difunctional group formation)

11) condensations.... H H

OH\_  |  |

a) Simple aldols : 2 CH3CHO -🡪 HO-C-CH­2-C=O

|

CH3

CH3 CH3

OH-| |

2(CH3)C=O ----🡪 HO-C-CH2-C=O

|

CH3

b) Mixed aldol: 2ArCHO + (CH3)2C=O 🡪 dibenzalacetone

c) Claisen (condensation with esters)

NaOEt + CH3C=O ----🡪 EtOH + CH2=C-CH2-C=O

| | |

OEt ONa Et