Organic Chemistry Lecture 3 – Carbonyls and Amines

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The Carbonyl Group

C=O bond with sp^2 hybridization and planar stereochemistry
Aldehyde has R-CO-H, ketone has R-CO-R

Oxygen has a partial negative charge, carbon has a partial positive charge (ELECTROPHILE)
Keto-enol tautomerization causes α-carbon to become a NUCLEOPHILE

Nucleophilic Addition

Aldehyde + alcohol -> hemiacetal
Ketone + alcohol -> hemiketal
Hemiacetal + alcohol -> acetal
Hemiketal + alcohol -> ketal

Aldehyde/ketone + diol -> protected from nucleophilic attack

Water + aldehyde/ketone -> geminal diol

Aldol condensation

Carbonyl (keto) + carbonyl (enol) -> aldol
Aldol + heat/base -> enal

Halogenation: Ketone + halogen -> adds to alpha carbon

Methyl ketone + 3 X_2 -> trihalogenated alpha carbon
Trihalogenated product + base -> carboxylic acid, haloform (HCX_3)

Wittig reaction: Ylide + carbonyl -> alkene

α-β unsaturated carbonyls: nucleophilic addition can happen at carbonyl, α, β carbons

Carboxylic Acids

High boiling point b/c of strong hydrogen bonds
Undergo nucleophilic substitution reactions

Decarboxylation
β-keto acid -> ketone + carbon dioxide

Carboxylic acid derivatives
CAD + $SOCl_2$/PCl_3/PCl_5 -> acyl chloride
CAD + ROH -> ester
CAD + RNH_2 -> amide
CAD + RCOOH -> anhydride
CAD + H_2O -> carboxylic acid

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Esterification: COOH + ROH -> COOR + H_2O
Transesterification: COOR + R'OH -> COOR' + ROH

Acetoacetic ester synthesis
H_3C-CO-CH_2-CO-OC_2H_5 + R-X -> H_3C-CO-CHR-CO-OC_2H_5
H_3C-CO-CHR-CO-OC_2H_5 + H^+/heat -> H_3C-CO-CH_2R + CO_2

Amines

Can have three or four bonds, act like weak bases

Amine + aldehyde/ketone -> (secondary) enamine N-C=C or (primary) imine N=C-C

Wolff-Kishner reduction: carbonyl + hydrazine H_2NNH_2 -> alkane

Alkylation: amine + R-X -> alkylated amine
Hofmann elimination: R_4N + heat -> alkenes
Hofmann product: major product, least stable product
Saytzeff product: minor product, most stable product

Diazotization: primary amine + N^+=O + H_2O + H^+ -> R-N(trip)N; can be used to add to benzyl

Amides
Hofmann degradation: R-CO-NH_2 + base -> R-NH_2 + CO_2