



Crack Notes [Organic Chem 3] Carbonyls & Amides

The Carbonyl Group

C=O bond with sp² 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 $\rightarrow$ hemiacetal

Ketone + alcohol $\rightarrow$ hemiketal

Hemiacetal + alcohol $\rightarrow$ acetal

Hemiketal + alcohol $\rightarrow$ ketal

Aldehyde/ketone + diol $\rightarrow$ protected from nucleophilic attack

Water + aldehyde/ketone $\rightarrow$ geminal diol

Aldol condensation

Carbonyl (keto) + carbonyl (enol) $\rightarrow$ aldol

Aldol + heat/base $\rightarrow$ enal

Halogenation: Ketone + halogen $\rightarrow$ adds to alpha carbon

Methyl ketone + 3 X₂ $\rightarrow$ trihalogenated alpha carbon

Trihalogenated product + base $\rightarrow$ carboxylic acid, haloform (HCX₃)

Wittig reaction: Ylide + carbonyl $\rightarrow$ 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 $\rightarrow$ ketone + carbon dioxide

Carboxylic acid derivatives

CAD + SOCl₂/PCl₃/PCl₅ $\rightarrow$ acyl chloride

CAD + ROH $\rightarrow$ ester

CAD + RNH₂ $\rightarrow$ amide

CAD + RCOOH $\rightarrow$ anhydride

CAD + H₂O $\rightarrow$ carboxylic acid



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Esterification: $\text{COOH} + \text{ROH} \rightarrow \text{COOR} + \text{H}_2\text{O}$

Transesterification: $\text{COOR} + \text{R}'\text{OH} \rightarrow \text{COOR}' + \text{ROH}$

Acetoacetic ester synthesis

$\text{H}_3\text{C-CO-CH}_2\text{-CO-OC}_2\text{H}_5 + \text{R-X} \rightarrow \text{H}_3\text{C-CO-CHR-CO-OC}_2\text{H}_5$

$\text{H}_3\text{C-CO-CHR-CO-OC}_2\text{H}_5 + \text{H}^+/\text{heat} \rightarrow \text{H}_3\text{C-CO-CH}_2\text{R} + \text{CO}_2$

Amines

Can have three or four bonds, act like weak bases

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

Wolff-Kishner reduction: carbonyl + hydrazine $\text{H}_2\text{NNH}_2 \rightarrow$ alkane

Alkylation: amine + $\text{R-X} \rightarrow$ alkylated amine

Hofmann elimination: $\text{R}_4\text{N} + \text{heat} \rightarrow$ alkenes

Hofmann product: major product, least stable product

Saytzeff product: minor product, most stable product

Diazotization: primary amine + $\text{N}^+=\text{O} + \text{H}_2\text{O} + \text{H}^+ \rightarrow \text{R-N(trip)N}$; can be used to add to benzyl

Amides

Hofmann degradation: $\text{R-CO-NH}_2 + \text{base} \rightarrow \text{R-NH}_2 + \text{CO}_2$