You should be able to answer questions about the following reaction types on exam 3.

### Oxidations

- Benzyl alcohol to benzaldehyde with KMnO₄
- Primary alcohol to 1-ketone with KMnO₄
- Primary alcohol to 2-ketone with KMnO₄ and CrO₃/H₃O⁺

### Reductions (Hydrides, Grignards and Gilman Reagents)

- Primary alcohol to primary alcohol with LiAlH₄ and then H₃O⁺
- Secondary alcohol to secondary alcohol with NaBH₄
- Secondary alcohol to secondary alcohol with LiAlH₄ and then H₃O⁺
- Primary alcohol to primary alcohol with BH₃
- Primary alcohol to primary alcohol with LiAlH₄ and then H₃O⁺
- Secondary alcohol to secondary alcohol with R'MgBr
- Secondary alcohol to secondary alcohol with R'₂CuLi
- Secondary alcohol to secondary alcohol with LiAlH₄, then H₃O⁺, and finally R'MgBr
- Secondary alcohol to secondary alcohol with DIBAL
- Primary alcohol to primary alcohol with LiAlH₄ and then H₃O⁺
Other Reactions of Aldehydes and Ketones

Wittig Reaction

\[
\begin{align*}
\text{Ph}_{3}P\text{=CH}_2 + \text{RO} &\rightarrow \text{Ph}_{3}P\text{=O} \\
\text{Ac} + \text{H}^+ + \text{R-NH}_2 &\rightarrow \text{R-NH} + \text{H}_2\text{O} \\
\text{Ac} + \text{R}_2\text{NH} &\rightarrow \text{H}_2\text{O} \\
\text{Ac} + 2\text{ROH} &\rightarrow \text{RO} + \text{RO} + \text{H}_2\text{O}
\end{align*}
\]

1,4-Addition

\[
\begin{align*}
\text{Ac} + \text{CH}_3\text{NH}_2 &\rightarrow \text{Ac-NHCH}_3 \\
\text{Ac} + \text{Ph}_2\text{CuLi} &\rightarrow \text{Ph}
\end{align*}
\]

1,2-Addition

\[
\begin{align*}
\text{Ac} + \text{PhMgBr} &\rightarrow \text{Ph} \\
\text{Ac} + \text{PhLi} &\rightarrow \text{Ph} \\
\text{Ac} + \text{NaBH}_4 &\rightarrow \text{H} \\
\text{Ac} + \text{LiAlH}_4 &\rightarrow \text{H}
\end{align*}
\]
Making Carboxylic Acids and Derivatives

\[
\text{MgBr} + \text{O} = \text{CO} \rightarrow \text{MgO} + \text{phenolate}
\]

Heat

\[
\text{R} - \text{OH} + \text{HO}_2\text{R} \rightarrow \text{R} - \text{O} - \text{R} + \text{H}_2\text{O}
\]

Carboxylic Acids

\[
\text{R} - \text{OH} \xrightarrow{\text{SOCI}_2} \text{R} - \text{Cl}
\]

\[
\text{R} - \text{OH} \xrightarrow{\text{NaOH then CH}_3\text{I}} \text{R} - \text{OCH}_3 \quad \text{limited to primary alkyl halides}
\]

\[
\text{R} - \text{OH} \xrightarrow{\text{HA, CH}_3\text{OH}} \text{R} - \text{OCH}_3 \quad \text{limited to inexpensive alcohol solvents - methanol and ethanol most practical}
\]

Acid Chlorides

\[
\text{R} - \text{Cl} \xrightarrow{\text{H}_2\text{O}} \text{R} - \text{OH} + \text{HCl}
\]

\[
\text{R} - \text{Cl} \xrightarrow{\text{R'}\text{CO}_2\text{Na}} \text{R} - \text{O} - \text{R'} + \text{NaCl}
\]

\[
\text{R} - \text{Cl} \xrightarrow{\text{R'}\text{OH, pyridine}} \text{R} - \text{O} - \text{R'} + \text{pyridine} \cdot \text{HCl}
\]

\[
\text{R} - \text{Cl} \xrightarrow{\text{R'}\text{NH}_2, pyridine}} \text{R} - \text{NHR'} + \text{pyridine} \cdot \text{HCl}
\]

Acid Anhydrides

\[
\text{R} - \text{O} - \text{O} \xrightarrow{\text{H}_2\text{O}} \text{R} - \text{OH} + \text{HO}_2\text{CCH}_3
\]

\[
\text{R} - \text{O} - \text{O} \xrightarrow{\text{R'}\text{OH, pyridine}} \text{R} - \text{O} - \text{R'} + \text{pyridine} \cdot \text{HO}_2\text{CCH}_3
\]

\[
\text{R} - \text{O} - \text{O} \xrightarrow{\text{R'}\text{NH}_2, pyridine}} \text{R} - \text{NHR'} + \text{pyridine} \cdot \text{HO}_2\text{CCH}_3
\]
Esters

\[
\text{RCOOCH}_3 + \text{H}_2\text{O, NaOH} \rightarrow \text{RCOOH} + \text{HOCH}_3
\]

then \(\text{H}_3\text{O}^+\)

Amides

\[
\text{RCONH}_2 + \text{H}_2\text{O, H}_3\text{O}^+ \rightarrow \text{RCOOH}
\]

heat

**NEED TO KNOW MECHANISM**

**Mechanism for Imine Formation**

Up to here this is identical to a hydration with amine as nucleophile instead of water

**NEED TO KNOW MECHANISM**

**Mechanism for Enamine Formation**

The only difference is this last step. There is no proton on the nitrogen to come off, so a proton is taken off of the alpha carbon
**NEED TO KNOW MECHANISM**

**Mechanism for Acetal Formation**

\[ \text{Formation of Acetal} \]

\[
\begin{align*}
\text{Acetaldehyde} & \xrightarrow{\text{HA}} \text{Formaldehyde} & & \text{Formaldehyde} & \xrightarrow{\text{HA}} \text{Hemiacetal} & & \text{Watersoluble} \\
\text{+ H}_2\text{O} & \xrightarrow{\text{A}} \text{Acetaldehyde} & & \text{Acetaldehyde} & \xrightarrow{\text{HA}} \text{Hemiacetal} & & \text{+ H}_2\text{O}
\end{align*}
\]

**NEED TO KNOW MECHANISM**

**Fischer Esterification**

\[ \text{Esterification} \]

\[
\begin{align*}
\text{Acetic Acid} & \xrightarrow{\text{HA}} \text{Acetylating Agent} & & \text{Acetylating Agent} & \xrightarrow{\text{HA}} \text{Ester} & & \text{Water} \\
\text{+ R'OH} & \xrightarrow{\text{A}} \text{Acetic Acid} & & \text{Acetic Acid} & \xrightarrow{\text{HA}} \text{Ester} & & \text{+ R'OH}
\end{align*}
\]
NEED TO KNOW MECHANISMS

Acid Catalyzed Hydrolysis

Base Catalyzed Hydrolysis (Saponification)

Rapid acid-base reaction takes place. Carboxylate is a thermodynamic sink and makes the reaction essentially non-reversible. To get the carboxylic acid, add acid to protonate.