

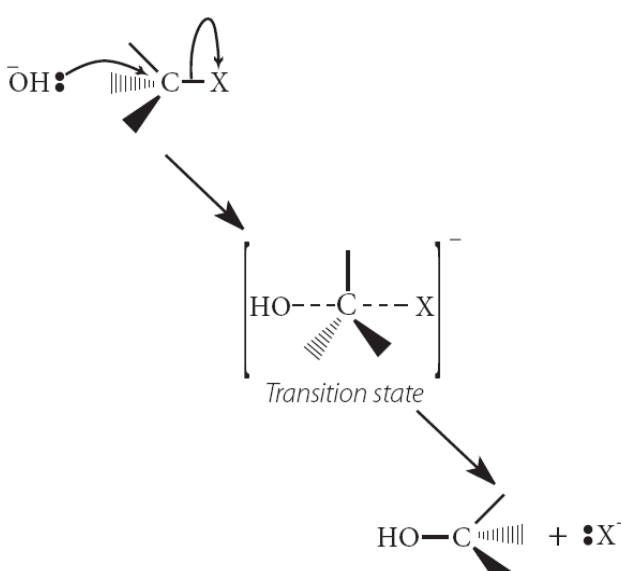
Organic Chemistry Review: Topic 10 & Topic 20

Organic Structure	Mechanism	Examples
Alkanes $C-C$ σ - bond	Substitution (Incoming atom or group will displace an existing atom or group in a molecule)	$Cl-Cl \longrightarrow Cl\cdot + \cdot Cl$ <p style="text-align: center;"><i>Figure 1016 - Initiation</i></p> $Cl\cdot + H-CH_3 \longrightarrow Cl-H + \cdot CH_3$ $\cdot CH_3 + Cl-Cl \longrightarrow CH_3-Cl + Cl\cdot$ <p style="text-align: center;"><i>Figure 1017 - Propagation</i></p> $Cl\cdot + \cdot Cl \longrightarrow Cl-Cl$ $Cl\cdot + \cdot CH_3 \longrightarrow CH_3-Cl$ $CH_3\cdot + CH_3\cdot \longrightarrow CH_3-CH_3$ <p style="text-align: right;">Occurs with exposure to ultraviolet light or sunlight, or high temperatures as the energy breaks the halogen covalent bond, X—X. Rate of reaction: $Cl_2 > Br_2 > I_2$</p>
Alkenes $C=C$ Π - bond	Addition	$\begin{array}{c} \diagup \quad \diagdown \\ C=C \\ \diagdown \quad \diagup \end{array} + Br_2 \longrightarrow \begin{array}{c} \quad \\ -C-C- \\ \quad \\ Br \quad Br \end{array}$ <p style="text-align: right;">Spontaneous, test for unsaturation, red-orange bromine liquid is decolourised in presence of unsaturated molecule.</p> $\begin{array}{c} \diagup \quad \diagdown \\ C=C \\ \diagdown \quad \diagup \end{array} + HCl \longrightarrow \begin{array}{c} \quad \\ -C-C- \\ \quad \\ H \quad Cl \end{array}$ <p style="text-align: right;">Spontaneous, (Hydrogen halide), recall Markovnikov's Rule</p> $\begin{array}{c} \diagup \quad \diagdown \\ C=C \\ \diagdown \quad \diagup \end{array} + H_2 \xrightarrow[\text{Catalyst}]{\text{Nickel}} \begin{array}{c} \quad \\ -C-C- \\ \quad \\ H \quad H \end{array}$ <p style="text-align: right;">Reduction: addition of hydrogen using nickel as catalyst at $150^\circ C$ (hydrogenation), heterogeneous catalysis.</p> $\begin{array}{c} \diagup \quad \diagdown \\ C=C \\ \diagdown \quad \diagup \end{array} + H_2O \rightleftharpoons \begin{array}{c} \quad \\ -C-C- \\ \quad \\ H \quad OH \end{array}$ <p style="text-align: right;">Needs acid (H_2SO_4 or H_3PO_4) or heated aluminum oxide catalyst (Al_2O_3) at high temperature ($\sim 300^\circ C$) and pressure (~ 7 atm)</p>
Alcohols $R-OH$		$C_2H_4(g) + H_2O(g) \xrightleftharpoons[\text{catalyst}]{H_3PO_4 \text{ or } Al_2O_3} C_2H_5OH(g)$ <p style="text-align: right;">Forward reaction: phosphoric acid catalyst at high pressure Reverse reaction: acid catalyst or aluminum oxide</p> $C_2H_5OH(l) \xrightarrow{\text{excess } H_2SO_4 \approx 170^\circ C} C_2H_4(g) + H_2O(l)$ <p style="text-align: right;">Dehydration reaction: concentrated sulphuric or phosphoric acid at $\sim 170^\circ C$</p>

Organic Chemistry Review: Topic 10 & Topic 20

		<div style="text-align: center;"> <p>Tertiary Alcohol</p> $\begin{array}{c} \text{C} \\ \\ \text{C}-\text{C}-\text{O}-\text{H} \\ \\ \text{C} \end{array} \longrightarrow \text{Not easily oxidised}$ <p>Secondary Alcohol</p> $\begin{array}{c} \text{H} \\ \\ \text{C}-\text{C}-\text{O}-\text{H} \\ \\ \text{C} \end{array} \longrightarrow \begin{array}{c} \text{Ketone} \\ \text{C}-\text{C}=\text{O} \\ \\ \text{C} \end{array} \longrightarrow \text{No further oxidation}$ <p>Primary Alcohol</p> $\begin{array}{c} \text{H} \\ \\ \text{C}-\text{C}-\text{O}-\text{H} \\ \\ \text{H} \end{array} \longrightarrow \begin{array}{c} \text{Aldehyde} \\ \text{C}-\text{C}=\text{O} \\ \\ \text{H} \end{array} \longrightarrow \begin{array}{c} \text{Carboxylic acid} \\ \text{C}-\text{C}=\text{O} \\ \\ \text{O}-\text{H} \end{array}$ <p>Figure 1025 The oxidation of alcohols</p> </div> <ul style="list-style-type: none"> - Tertiary alcohol: No reactive hydrogen atoms so they don't readily oxidise. - Secondary alcohol: One reactive hydrogen and undergo one stage of oxidation to yield ketones. - Primary alcohol: Two reactive hydrogen and undergo two stages of oxidation to produce aldehydes and then carboxylic acids. <ul style="list-style-type: none"> • To obtain the aldehyde, the alcohol is added to the boiling oxidising agent so that it distils (distillation). • To oxidize the primary alcohol to the carboxylic acid, a higher concentration of the oxidising agent is used and the solution is refluxed (reflux). • Acidified potassium dichromate (VI) is usually used as the oxidising agent, changes colour from orange, Cr⁶⁺ to green Cr³⁺. <p>Recall:</p> <ul style="list-style-type: none"> - Oxidation = addition of oxygen or removal of hydrogen - Reduction = addition of hydrogen or removal of oxygen
<p>Halogenoalkanes R-X</p>	<p>Nucleophilic Substitution</p>	<ul style="list-style-type: none"> - Nucleophile = an atom or group that is an electron pair donor and forms a co-ordinate bond. <div style="text-align: center;"> $\begin{array}{ccc} \begin{array}{c} \text{H} \\ \\ \text{C}-\text{C}-\text{X} \\ \\ \text{H} \end{array} & \begin{array}{c} \text{H} \\ \\ \text{C}-\text{C}-\text{X} \\ \\ \text{C} \end{array} & \begin{array}{c} \text{C} \\ \\ \text{C}-\text{C}-\text{X} \\ \\ \text{C} \end{array} \\ \text{Primary} & \text{Secondary} & \text{Tertiary} \end{array}$ <p>Figure 1030 Classes of halogenoalkanes</p> </div> <ul style="list-style-type: none"> - Tertiary halogenoalkanes undergo S_N1 (substitution, nucleophilic, unimolecular) mechanisms: <div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;"> $\begin{array}{c} \diagup \\ \\ \text{C}-\text{X} \\ \diagdown \end{array} \longrightarrow \begin{array}{c} \diagup \\ \\ \text{C}^+ \\ \diagdown \end{array} + \text{:X}^- \quad (\text{slow})$ <p>Carbocation intermediate</p> </div> <div style="text-align: center;"> $\begin{array}{c} \diagup \\ \\ \text{C}^+ \\ \diagdown \end{array} + \text{:OH}^- \longrightarrow \begin{array}{c} \diagup \\ \\ \text{C}-\text{OH} \\ \diagdown \end{array} \quad (\text{fast})$ </div> <div style="text-align: left; padding-left: 20px;"> <p>Slow rate determining step, unimolecular, heterolytic fission of the carbon-halogen bond to yield an electron deficient carbocation intermediate.</p> <p>Quick reaction with the hydroxide ion to form the final product.</p> </div> </div> <p style="text-align: right;">Rate = k [R-X]¹</p>

Organic Chemistry Review: Topic 10 & Topic 20

		<p>- Secondary halogenoalkanes undergo S_N1 and S_N2 mechanisms</p> <p>- Primary halogenoalkanes undergo S_N2 (substitution, nucleophilic, bimolecular) mechanisms:</p> <div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;">  </div> <div style="width: 30%;"> <p>The bimolecular attack of the hydroxide ion on the halogenoalkane molecules is the rate-determining step. Rate = k [R-X]¹[OH-]¹</p> <p>The bond to the hydroxide ion starts to form at the same time as the bond to the halogen breaks.</p> <p>Inversion of configuration results.</p> </div> </div>
<p>Nucleophilic Substitution Reactions (in depth)</p>		<p>- S_N1 mechanism:</p> <ul style="list-style-type: none"> • Slow heterolytic fission of the carbon-halogen bond to form a carbocation intermediate (rate determining step) • Intermediate reacts rapidly with the nucleophile to form the final product <p>- S_N2 mechanism:</p> <ul style="list-style-type: none"> • Breaking of the carbon-hydrogen bond occurs simultaneously with the formation of the new bond to the nucleophile • The rate at which these reactions occur depends on the nature of both the nucleophile and the halogenoalkanes; therefore S_N2 mechanisms occur more rapidly in aqueous alkali than in neutral solution <p>- The nature of the halogen affects the rate of reaction:</p> <ol style="list-style-type: none"> 1. As the halogen goes down the group (Cl, Br, I), the polarity of the carbon-halogen bond decreases and decreases the rate of reaction because the partial positive charge on the carbon would become smaller. 2. The decreasing strength of the carbon-halogen bond due to decreasing polarity going from chlorine to iodine increases the rate of reaction. <div style="text-align: center; margin-top: 20px;"> <p>C—Cl C—Br C—I</p> <p>—————→</p> <p>Decreasing polarity of C—X bond Decreasing strength of C—X bond Increasing rate of reaction</p> <p><i>Figure 1035 Effect of the halogen on the rate of nucleophilic substitution</i></p> </div>

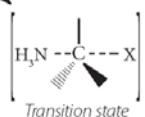
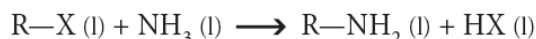
Organic Chemistry Review: Topic 10 & Topic 20

3. The bond strength is the dominant factor though so an overall increase of the rate of reaction takes place.
- Tertiary halogenoalkanes react by S_N1 mechanisms and primary halogenoalkanes react by S_N2 mechanisms because:
 - Tertiary carbocations are relatively stable because of the **positive inductive effect** of the alkyl groups, which reduces the charge on the central carbon, so stabilising the carbocation intermediate required for S_N1 .
 - The change from tetrahedral to trigonal planar geometry when the carbocation is formed increases the bond angle from 109° to 120° . In tertiary halogenoalkanes, this allows the alkyl groups to move further apart, stabilising the carbocation by reducing steric stress.
 - In the S_N2 mechanism, the nucleophile usually attacks the central carbon from the direction opposite to the halogen while in tertiary compounds bulky alkyl groups hinder such an attack.
 - S_N1 reactions generally occur faster than S_N2 reactions and thus the rate of hydrolysis of halogenoalkanes decreases in the order:

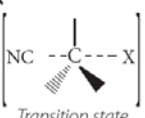
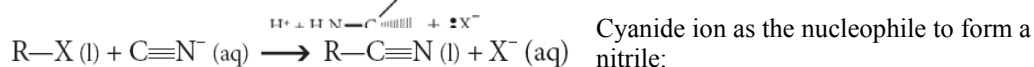
Tertiary > Secondary > Primary

- Nucleophilic substitution reactions can also react with:

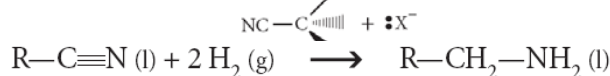
- **Ammonia, $:NH_3$, as the nucleophile to form a primary amine:**



S_N2 mechanism

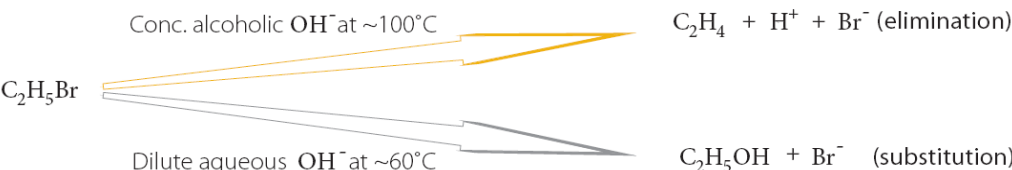
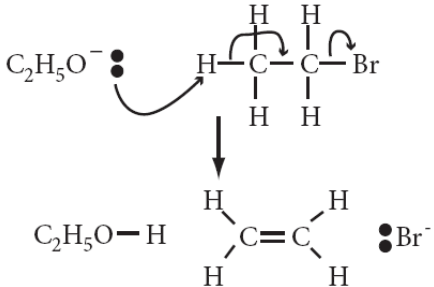
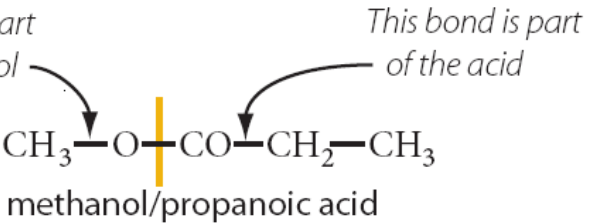


S_N2 mechanism: The triple bond in the nitrile may be readily reduced using hydrogen and a nickel catalyst to form a primary amine or oxidized to form a carboxylic acid. This is a very useful method to **ascend** the homologous series.

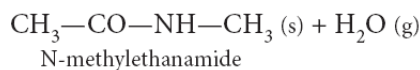
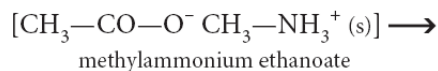
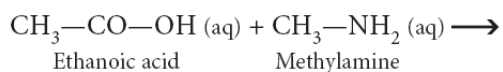


This amine has one more carbon than the one formed directly with ammonia.

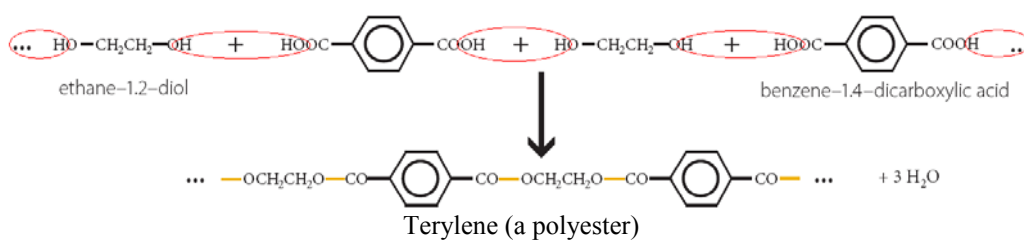
Organic Chemistry Review: Topic 10 & Topic 20

<p>Elimination Reactions (in depth)</p>	<div style="text-align: center;">  </div> <ul style="list-style-type: none"> - If a bromoalkane is warmed with dilute aqueous alkali at ~60°C, it undergoes substitution. - If a bromoalkane is warmed with a concentrated aqueous alkali at ~100°C, it undergoes elimination. $\text{C}_2\text{H}_5\text{OH} + \text{OH}^- \rightleftharpoons \text{C}_2\text{H}_5\text{O}^- + \text{H}_2\text{O}$ <p>The hydroxide ion reacts with the ethanol to produce the ethoxide ion above.</p> <ul style="list-style-type: none"> - The ethoxide ion is a stronger base and weaker nucleophile than the hydroxide ion and thus favours the elimination reaction, as does the higher temperature and concentration. <div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;">  </div> <div style="width: 40%;"> <p>The ethoxide ion acts as a base and removes the hydrogen ion from the carbon next to the halogen.</p> <p>Then the bromide is eliminated. If the halogen (bromine) is in the middle then elimination can occur in more than one direction and a mixture of products may result.</p> </div> </div>
<p>Condensation Reactions (in depth)</p>	<ul style="list-style-type: none"> - When alcohols are heated with carboxylic acids in the presence of concentrated sulphuric acid, they produce sweet smelling esters. <p style="background-color: yellow;">Ester = alcohol + carboxylic acid + heat + concentrated sulphuric acid</p> <p>Esterification reaction:</p> $\text{CH}_3\text{-CO-OH} + \text{CH}_3\text{-CH}_2\text{-OH}$ <p style="text-align: center;">ethanoic acid ethanol</p> $\xrightleftharpoons[\text{catalyst}]{\text{H}_2\text{SO}_4}$ $\text{CH}_3\text{-CO-O-CH}_2\text{-CH}_3 + \text{H}_2\text{O}$ <p style="text-align: right;">The hydrogen ions in the sulphuric acid acts as a catalyst to increase the rate of reaction and also acts as a dehydrating agent, thus shifts the equilibrium to the right, ensuring a good yield of product. Esters do not have an -OH group so they don't dissolve in water.</p> <ul style="list-style-type: none"> - Naming of esters: <div style="text-align: center;"> <p><i>This bond is part of the alcohol</i></p>  <p><i>This bond is part of the acid</i></p> <p>CH₃-O-CO-CH₂-CH₃ methanol/propanoic acid</p> <p>The molecule is methyl propanoate.</p> </div> <p>Ammonia and primary amines react with carboxylic acids to form a salt of the acid. If this is heated, it dehydrates to form an amide.</p>

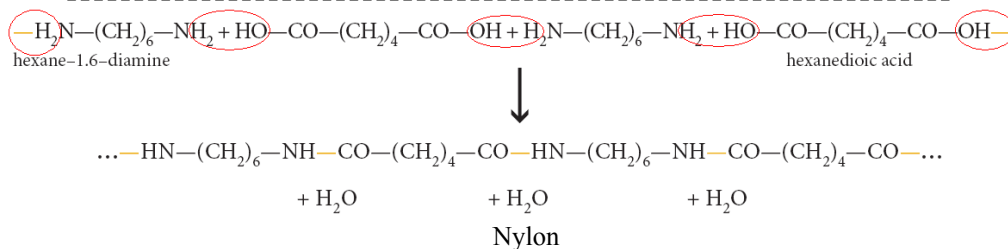
Organic Chemistry Review: Topic 10 & Topic 20



- The above reactions are used to make condensation polymers.
- Different functional groups are required and for each new bond between the monomer units (shown coloured below), a small molecule (often water) is produced.



The repeating unit in Terylene is: $[-\text{O—CH}_2\text{—CH}_2\text{—O—CO—C}_6\text{H}_4\text{—CO—}]$



The repeating unit in Nylon is: $[\text{HN—(CH}_2\text{)}_6\text{—NH—CO—(CH}_2\text{)}_4\text{—CO}]$

- Both are used to make cloth for garments