

FIVE TYPES OF REACTIONS

COMMENTS:

- It is very easy to distinguish between the first 3 types of reactions.

Addition	Elimination	Substitution
= $\longrightarrow$ — <i>double</i> <i>single</i> bond bond in reactant in product	— $\longrightarrow$ = <i>single</i> bond <i>double</i> in reactant bond in product	— $\longrightarrow$ — <i>single</i> bond <i>single</i> bond in reactant in product

- Note the difference between dehydrohalogenation and hydrolysis. In both a haloalkane is treated with a strong base. (such as NaOH or KOH).

- Dehydrohalogenation:** Treat haloalkane with

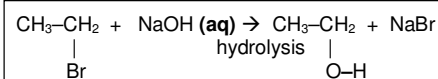
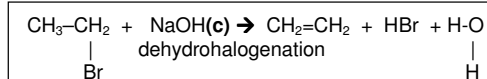
CONCENTRATED NaOH:

Elimination with alkene as product.

- Hydrolysis:** Treat haloalkane with

DILUTED NaOH in ethanol:

Substitution with alcohol as product.

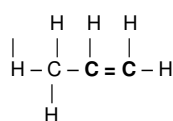


1. ADDITION

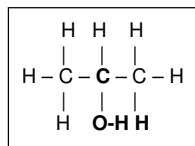
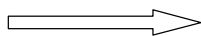
- Addition takes place when a atom/group is **added** to the organic molecule.
- It takes place in **unsaturated** molecules with double and triple bonds (alkenes and alkynes).

TYPE of ADDITION	ADDITION OF	EXAMPLE
Halogenation	Addition of halogen Cl_2/Br_2	$\begin{array}{c} \text{H} & \text{H} \\ & \\ \text{H}-\text{C} & =\text{C}-\text{H} \end{array} + \text{Br}-\text{Br} \rightarrow \begin{array}{c} \text{H} & \text{H} \\ & \\ \text{H}-\text{C} & -\text{C}-\text{H} \\ & \\ \text{Br} & \text{Br} \end{array}$
	Add halogen to alkene. This is a spontaneous reaction at room temperature.	
Hydrogenation	Addition of H_2	$\begin{array}{c} \text{H} & \text{H} \\ & \\ \text{H}-\text{C} & =\text{C}-\text{H} \end{array} + \text{H}-\text{H} \xrightarrow{\text{Pt}} \begin{array}{c} \text{H} & \text{H} \\ & \\ \text{H}-\text{C} & -\text{C}-\text{H} \\ & \\ \text{H} & \text{H} \end{array}$
	Use a Pt/Ni/Pd catalyst. Dissolve alkene in a non-polar solvent.	
Hydration	Addition of water	$\begin{array}{c} \text{H} & \text{H} \\ & \\ \text{H}-\text{C} & =\text{C}-\text{H} \end{array} + \begin{array}{c} \text{H} \\ \\ \text{O}-\text{H} \end{array} \xrightarrow{\text{H}_2\text{SO}_4} \begin{array}{c} \text{H} & \text{H} \\ & \\ \text{H}-\text{C} & -\text{C}-\text{H} \\ & \\ \text{H} & \text{O}-\text{H} \end{array}$
	Add excess H_2O to alkene with strong acid (H_2SO_4 or H_3PO_4) as catalyst.	
Hydrohalogenation	Addition of HCl/HBr/HI (hydrohalogens)	$\begin{array}{c} \text{H} & \text{H} \\ & \\ \text{H}-\text{C} & =\text{C}-\text{H} \end{array} + \text{H}-\text{Br} \rightarrow \begin{array}{c} \text{H} & \text{H} \\ & \\ \text{H}-\text{C} & -\text{C}-\text{H} \\ & \\ \text{H} & \text{Br} \end{array}$
	Add HCl/HBr/HI to alkene. NO WATER.	

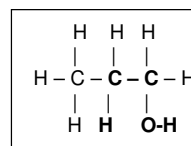
- Hydrogenation is used in the manufacturing of margarine from plant oils (like sunflower and canola). In the process the double bonds in the oils are converted into more saturated compounds. (The oils are “solidified”).
- Use the **Markovnikov rule** for the **main product** if 2 products are possible: in the main product the halogen or the OH group adds to the C atom with the most side chains, $\therefore$ **tertiary** (and not secondary) or **secondary** (and not primary). It is sometimes easier to apply Markovnikov's rule in terms of H's: H will attach to the C that already has the most Hs.



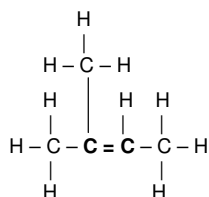
Hydration of prop-1-ene



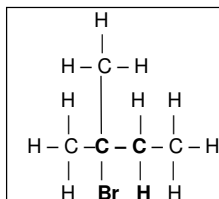
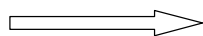
Main product is secondary alcohol



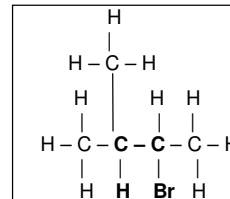
By product is Primary alcohol



Hydrohalogenation of 2-methylbut-2-ene (+ HBr)



Main product is Tertiary haloalkane



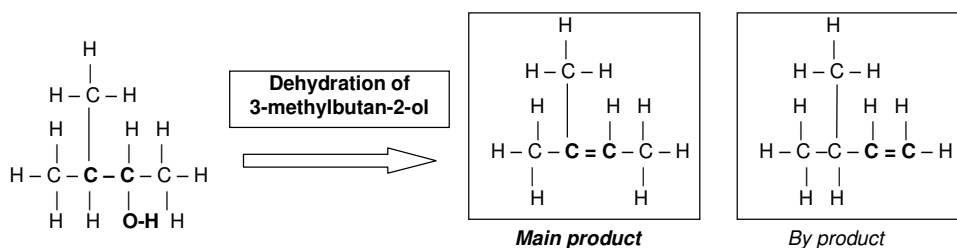
By product is Secondary haloalkane

2. ELIMINATION

- Elimination takes place when a molecule is **removed** from a organic molecule.
- It takes place in **saturated** molecules: alkanes, alcohols, haloalkanes.
- The product is always an alkene.

TYPE of ELIMINATION	ELIMINATION OF ...	EXAMPLE
Dehydration	Elimination of water from an alcohol	$ \begin{array}{c} \text{H} & \text{H} \\ & \\ \text{H}-\text{C}-\text{C}-\text{H} \\ & \\ \text{H} & \text{O-H} \end{array} \xrightarrow{\Delta, \text{H}_2\text{SO}_4} \begin{array}{c} \text{H} & \text{H} \\ & \\ \text{H}-\text{C}=\text{C}-\text{H} \end{array} + \begin{array}{c} \text{H} \\ \\ \text{O-H} \end{array} $
	Heat with concentrated H_2SO_4 (or H_3PO_4) as a catalyst.	
Dehydrohalogenation	Elimination of HCl/HBr/HI from a haloalkane	$ \begin{array}{c} \text{H} & \text{H} \\ & \\ \text{H}-\text{C}-\text{C}-\text{H} \\ & \\ \text{H} & \text{Br} \end{array} \xrightarrow{\Delta, \text{NaOH}} \begin{array}{c} \text{H} & \text{H} \\ & \\ \text{H}-\text{C}=\text{C}-\text{H} \end{array} + \text{H-Br} $
	OR	$ \begin{array}{c} \text{H} & \text{H} \\ & \\ \text{H}-\text{C}-\text{C}-\text{H} \\ & \\ \text{H} & \text{Br} \end{array} + \text{NaO-H} \rightarrow \begin{array}{c} \text{H} & \text{H} \\ & \\ \text{H}-\text{C}=\text{C}-\text{H} \end{array} + \begin{array}{c} \text{H} \\ \\ \text{O-H} \end{array} + \text{NaBr} $
Cracking of alkanes (fuel industry)	A long alkane is broken into - a shorter alkane and - a shorter alkene	2 possible crackings of butane: $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 \rightarrow \text{CH}_4 + \text{CH}_2=\text{CH}-\text{CH}_3$ $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 \rightarrow \text{CH}_3\text{CH}_3 + \text{CH}_2=\text{CH}_2$
	Thermal cracking: High pressure and high temperature, without a catalyst. Catalytic cracking: Low temperature with a catalyst.	

- Use the **Zaitsev rule** for the **main product** if two products are possible: the main product contains the more highly substituted double bond, (e.g. double bond rather forms “in the middle” and not “on the tip”).



3. SUBSTITUTION

- Substitution takes place when an atom/group is **replaced** by another atom/group.
- It takes place in **saturated** molecules: alkanes, alcohols and halo alkanes.

TYPE of SUBSTITUTION	... IS REPLACED BY...	EXAMPLE
Alkane + halogen	H is replaced by Cl/Br (only a single H)	$ \begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{H} - \text{C} - \text{C} - \text{H} \\ \quad \\ \text{H} \quad \text{H} \\ \text{alkane} \end{array} + \text{Br}-\text{Br} \xrightarrow{\text{light}} \begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{H} - \text{C} - \text{C} - \text{H} \\ \quad \\ \text{H} \quad \text{Br} \\ \text{haloalkane} \end{array} + \text{H}-\text{Br} $
Reaction is slow, will only take place in sunlight (hf) (or heated (Δ)).		
Haloalkane + KOH Hydrolysis: reaction of a compound with water	Cl/Br is replaced by OH	$ \begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{H} - \text{C} - \text{C} - \text{H} \\ \quad \\ \text{H} \quad \text{Br} \end{array} + \text{NaO}-\text{H} \xrightarrow{\Delta} \begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{H} - \text{C} - \text{C} - \text{H} \\ \quad \\ \text{H} \quad \text{O}-\text{H} \end{array} + \text{NaBr} $
Dissolve haloalkane in ethanol. Strong base like NaOH or KOH is dissolved in ethanol, added to the haloalkane, and heated.		
With H₂O hydrolysis also takes place, but slower.		$ \begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{H} - \text{C} - \text{C} - \text{H} \\ \quad \\ \text{H} \quad \text{Br} \end{array} + \text{O}-\text{H} \xrightarrow{\Delta} \begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{H} - \text{C} - \text{C} - \text{H} \\ \quad \\ \text{H} \quad \text{O}-\text{H} \end{array} + \text{H}-\text{Br} $
Dissolve haloalkane in ethanol. Add water.		
Alcohol + HCl/HBr/HI	OH is replaced by Cl/Br	$ \begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{H} - \text{C} - \text{C} - \text{H} \\ \quad \\ \text{H} \quad \text{O}-\text{H} \end{array} + \text{H}-\text{Br} \xrightarrow{\text{NaBr, H}_2\text{SO}_4} \begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{H} - \text{C} - \text{C} - \text{H} \\ \quad \\ \text{H} \quad \text{Br} \end{array} + \text{H}-\text{O} \begin{array}{c} \text{H} \\ \\ \text{H} \end{array} $
• <u>Primary and secondary alcohols</u>: Add solid NaBr (or KBr) with concentrated H₂SO₄ as catalyst. (The alcohol then reacts with HBr which forms from NaBr and H₂SO₄.) High temperature used. • <u>Tertiary alcohols</u>: Add alcohol to HBr at room temperature. I.e. 2-methylbutan-2-ol changed into 2-bromo-2-methylbutane		

4. COMBUSTION (OXIDATION)

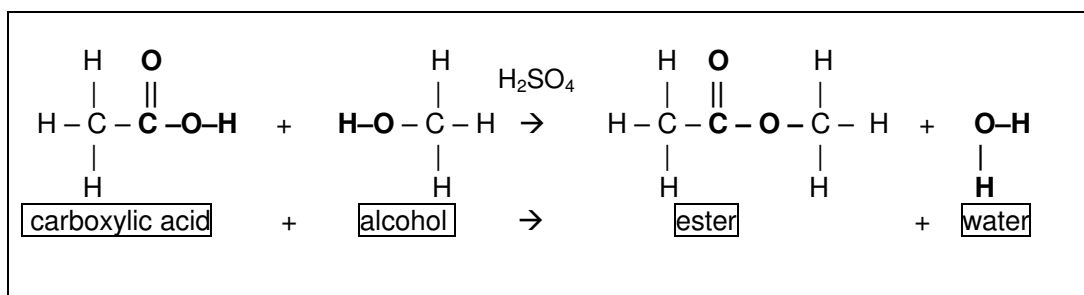
- The alkanes are **fossil fuels**, and crude oil is a natural mixture of alkanes. E.g. petrol, diesel and jet fuel are all natural alkanes.
- Alkanes (fossil fuels) **react with oxygen** during combustion.
The combustion yields CO_2 (carbon dioxide) in EXCESS oxygen, and H_2O .
The combustion yields CO (carbon monoxide) in LIMITED oxygen, and H_2O .
 CO_2 , CO and H_2O are inorganic products.
- These reactions are highly exothermic.
- These reactions are written in molecular formulae.
- E.g. combustion of propane: $\text{C}_3\text{H}_8 + 5\text{O}_2 \rightarrow 3\text{CO}_2 + 4\text{H}_2\text{O}$

To balance a combustion reaction:

- Write a "2" in front of the hydrocarbon.
- Balance C.
- Balance H.
- Then only balance O.
- Check if coefficients can be divided by 2, as coefficients should be in their lowest ratio.

5. ESTERIFICATION (CONDENSATION)

- Carboxylic acid react with alcohols and yields esters and H_2O .
- The reaction takes place in the presence of concentrated H_2SO_4 as catalyst.
- Example: The preparation of methyl ethanoate:



POSSIBLE REACTIONS PER HOMOLOGOUS SERIES

- **ALKANES**

- **Combustion:** Reaction with oxygen;
- **Substitution:** Reaction with halogens;
- **Elimination:** Cracking.

- **ALKENES**

- **Addition:**
 - Halogenation: Addition of halogens;
 - Hydrogenation: Addition of hydrogen;
 - Hydration: Addition of water;
 - Hydrohalogenation: Addition of a hydrogen halide.

- **ALCOHOLS**

- **Elimination:** Dehydration – elimination of water;
- **Substitution:** Reaction with a hydrogen halide;
- **Esterification:** Reaction with carboxylic acids.

- **HALOALKANES**

- **Elimination:** Dehydrohalogenation – elimination of hydrogen halide;
- **Substitution:** Reaction with strong base (like NaOH).

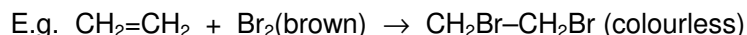
- **CARBOXYLIC ACIDS**

- **Esterification:** Reaction with alcohols.

DISTINGUISH BETWEEN SATURATED AND UNSATURATED MOLECULES

Method to test if a compound is saturated (alkane), or unsaturated (alkene): Add the unknown compound to bromine. The rate at which the bromine loses its colour determines if the added compound is saturated or unsaturated.

- Unsaturated molecules (alkenes) react spontaneously and quickly with bromine.
 - After adding the bromine, the brown colour of the bromine disappears immediately. It shows that the unsaturated molecule reacts spontaneously with bromine and yields colourless products.
 - The reaction is halogenation (addition).



- Saturated molecules (alkanes) do not react with bromine.
 - The brown colour of bromine remains unchanged. Only in light and after a while some discolouring takes place. It shows that the saturated molecule reacts non-spontaneously with bromine and yields colourless products.
 - The reaction is substitution.

