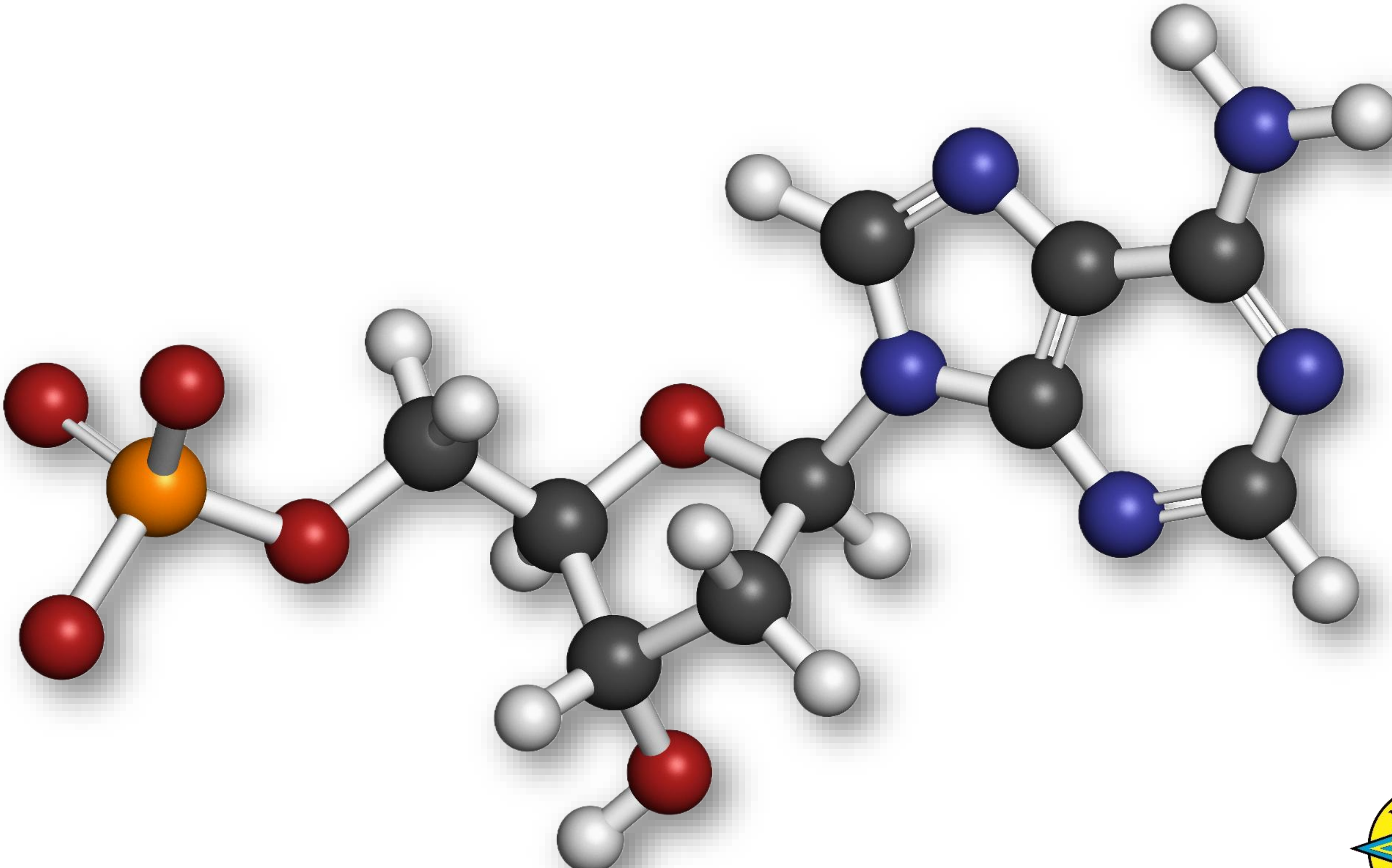
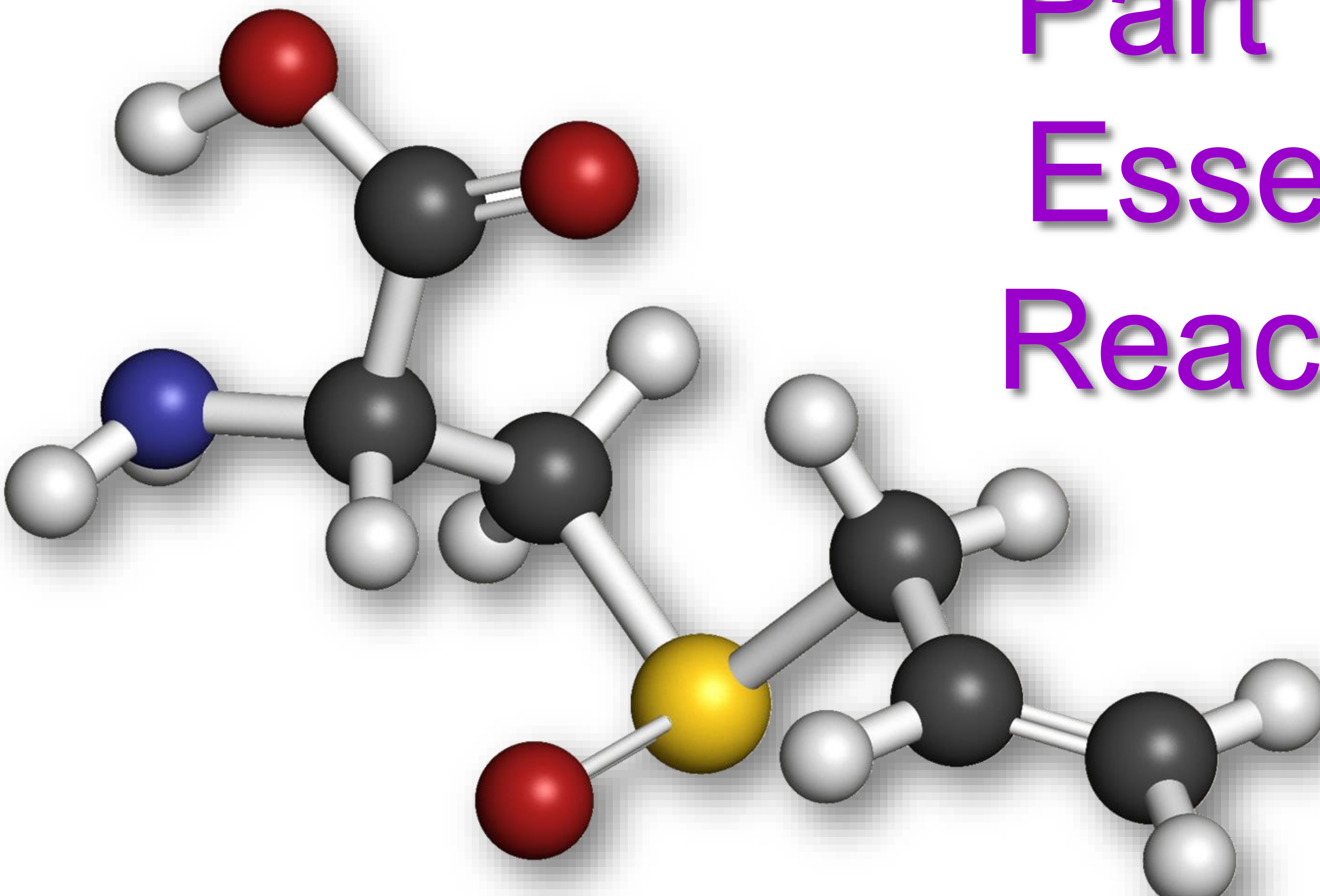
Organic Chemistry



Organic Chemistry

Part Two: Essential Reactions



Organic Chemistry

How are the reactions of organic compounds *classified*?

Organic Chemistry

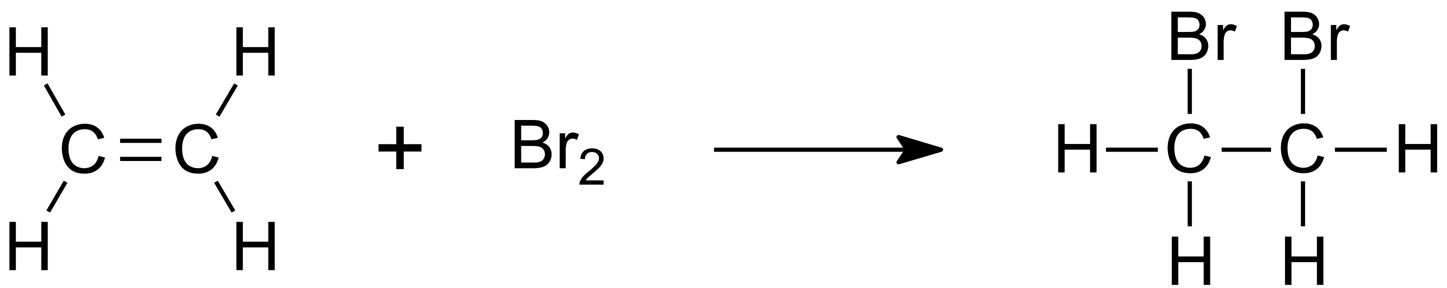
Classification of Organic Reactions

Organic reactions can be classified into (at least) three main types:

- Addition.
- Elimination.
- Substitution.

Organic Chemistry

Classification of Organic Reactions



Ethene

1,2-Dibromoethane

Unsaturated

Saturated

Organic Chemistry

Classification of Organic Reactions

Ethene

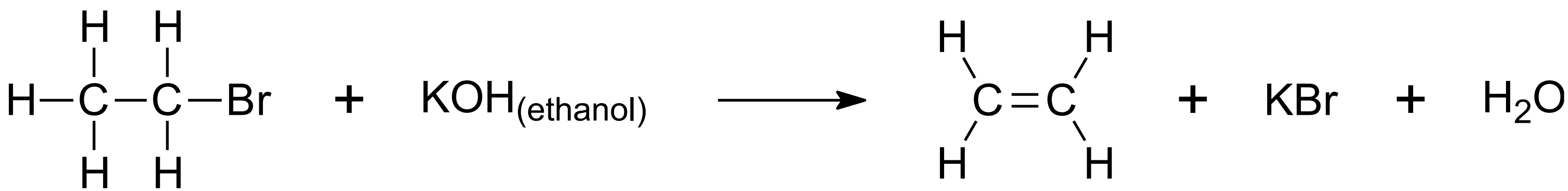
1,2-Dibromoethane

Unsaturated

Saturated

Organic Chemistry

Classification of Organic Reactions



Bromoethane

Ethene

Saturated

Unsaturated

Organic Chemistry

Classification of Organic Reactions

Bromoethane

Ethene

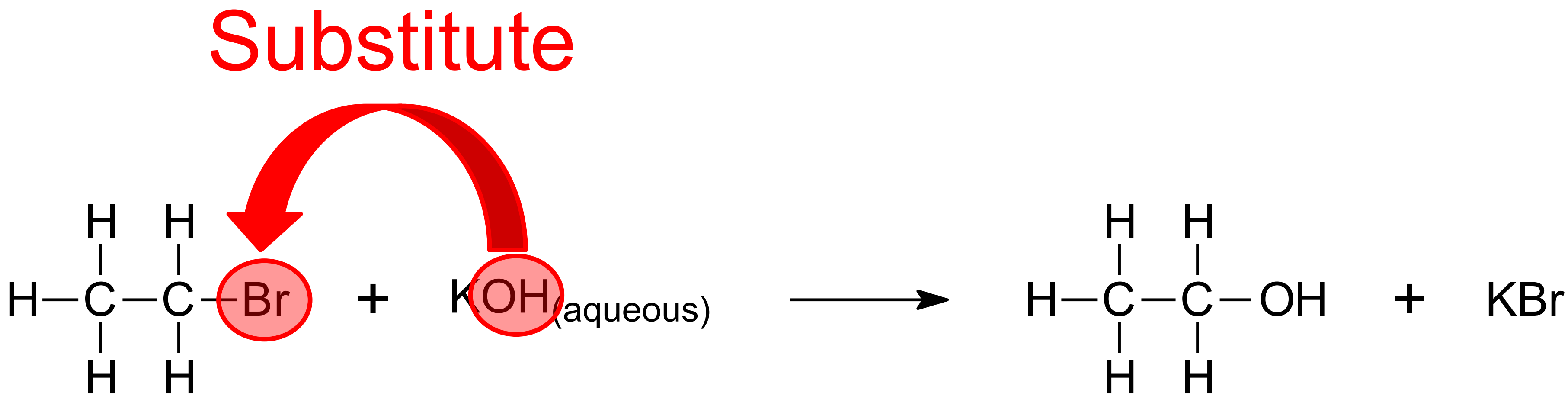
Elimination

Saturated

Unsaturated

Organic Chemistry

Classification of Organic Reactions

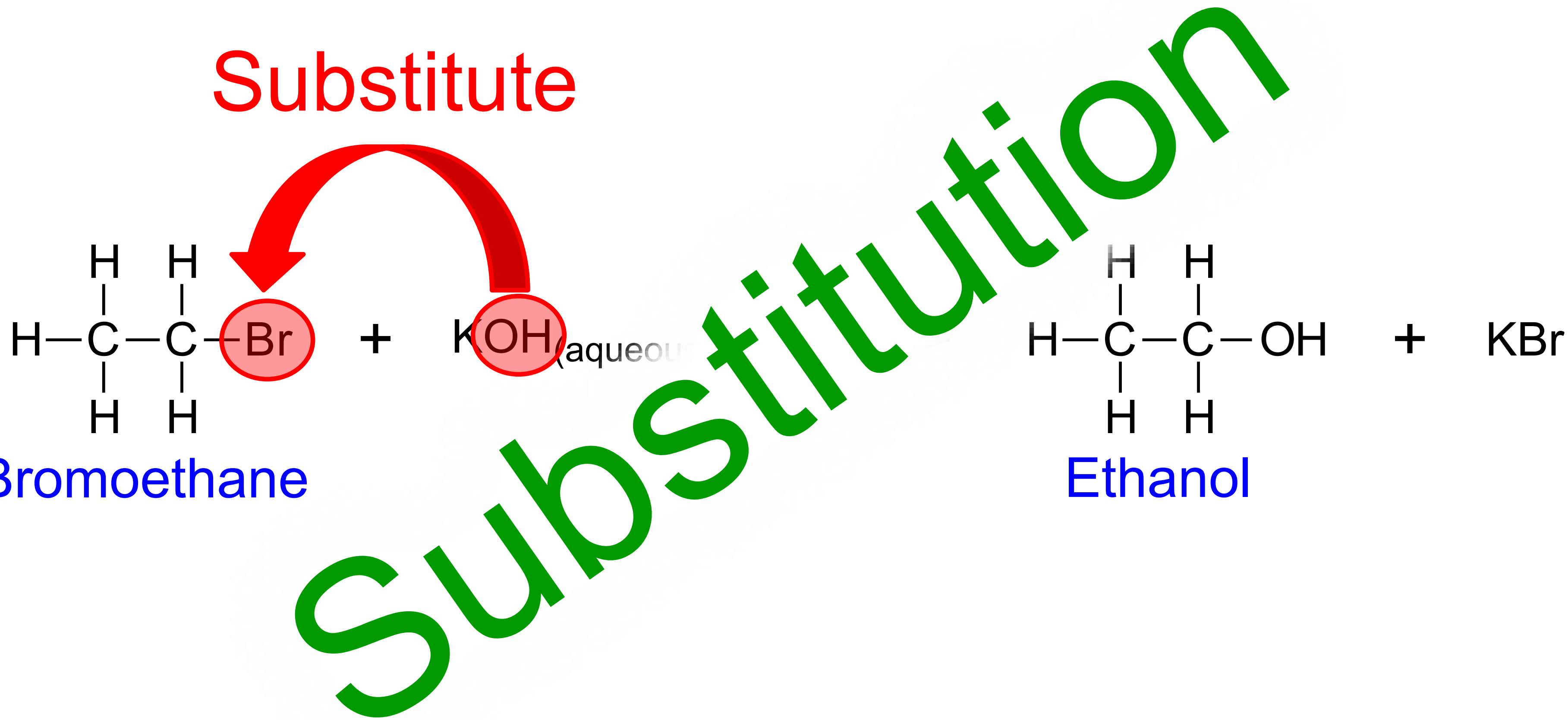


Bromoethane

Ethanol

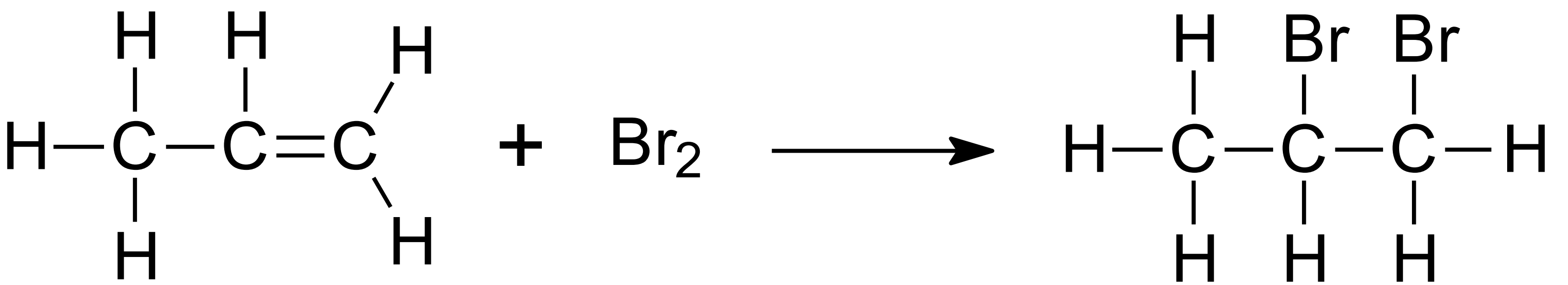
Organic Chemistry

Classification of Organic Reactions



Organic Chemistry

Classification of Organic Reactions



Propene

1,2-Dibromopropane

Organic Chemistry

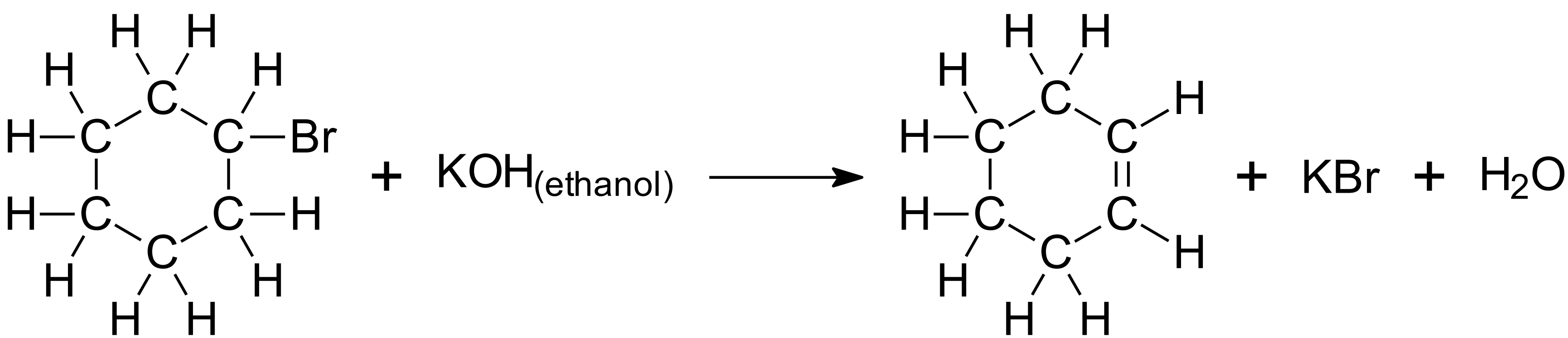
Classification of Organic Reactions

Propene

1,2-Dibromopropane

Organic Chemistry

Classification of Organic Reactions



Bromo-cyclohexane

Cyclohexene

Organic Chemistry

Classification of Organic Reactions

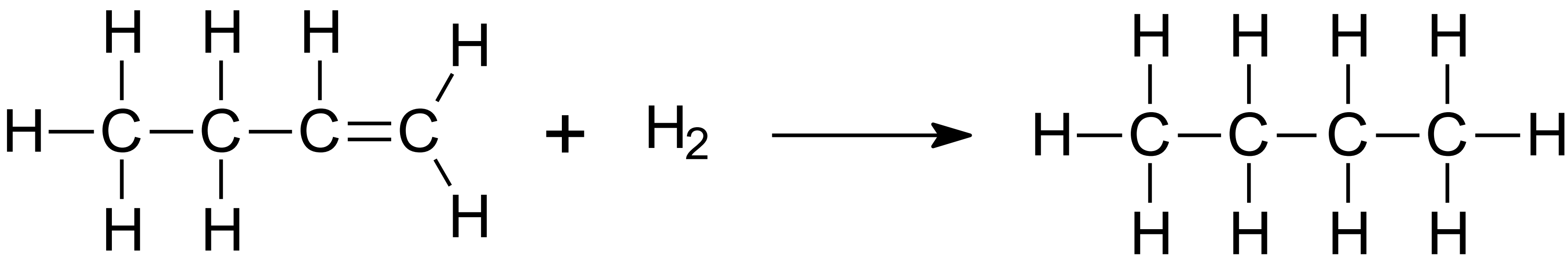
Bromo-cyclohexan

Cyclohexene

Elimination

Organic Chemistry

Classification of Organic Reactions



But-1-ene

Butane

Organic Chemistry

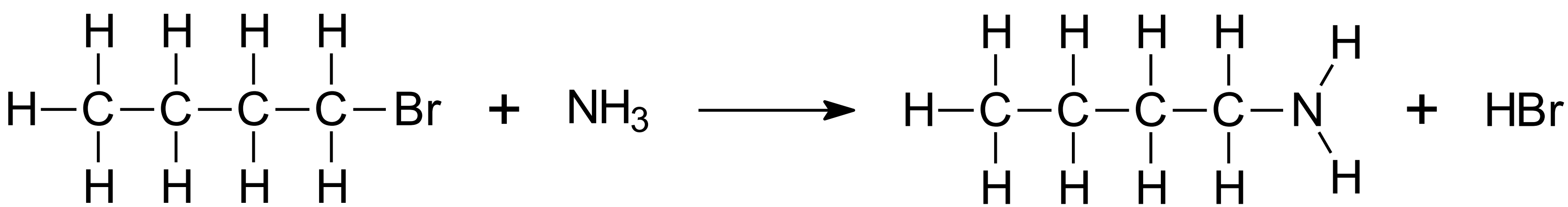
Classification of Organic Reactions

But-1-ene

Butane

Organic Chemistry

Classification of Organic Reactions



1-Bromobutane

Butyl-1-amine

Organic Chemistry

Classification of Organic Reactions

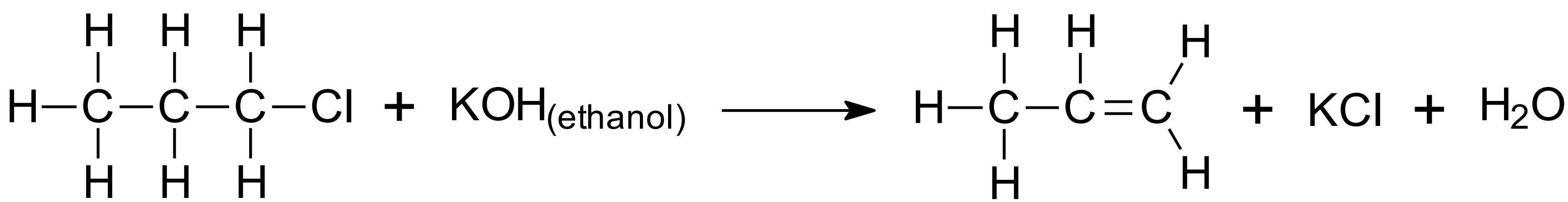
Substitution

1-Bromobutane

Butyl-1-amine

Organic Chemistry

Classification of Organic Reactions



1-Chloropropane

Propene

Organic Chemistry

Classification of Organic Reactions

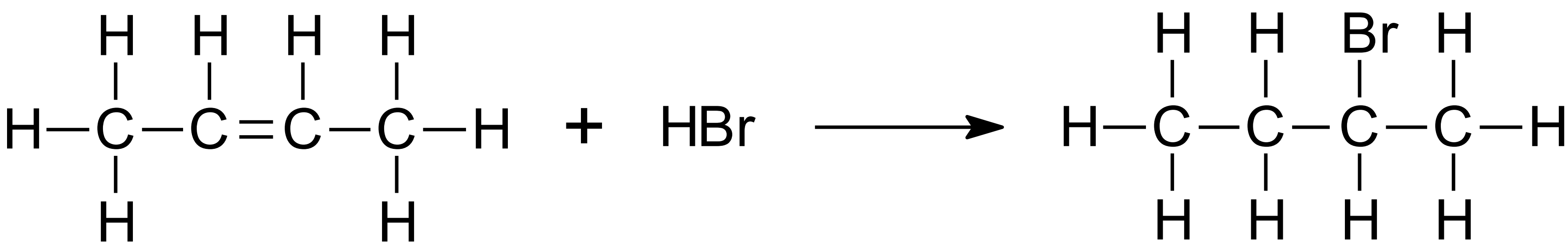
1-Chloropropane

Propene

Elimination

Organic Chemistry

Classification of Organic Reactions



But-2-ene

2-Bromobutane

Organic Chemistry

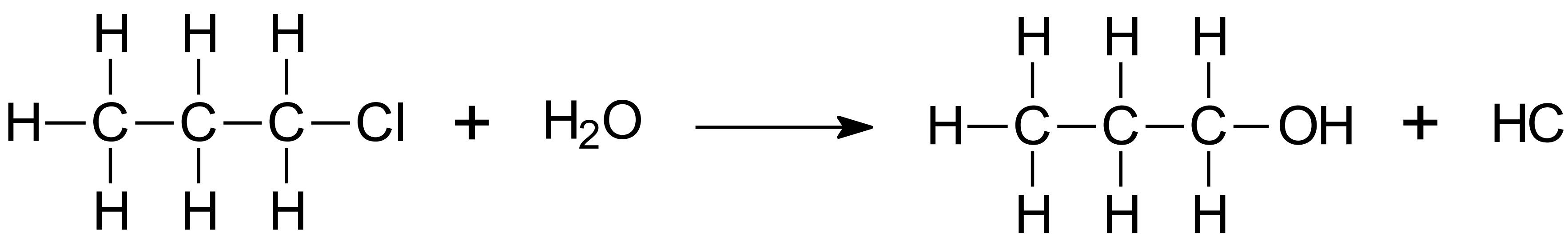
Classification of Organic Reactions

But-2-ene

2-Bromobutane

Organic Chemistry

Classification of Organic Reactions



1-Chloropropane

Propan-1-ol

Organic Chemistry

Classification of Organic Reactions

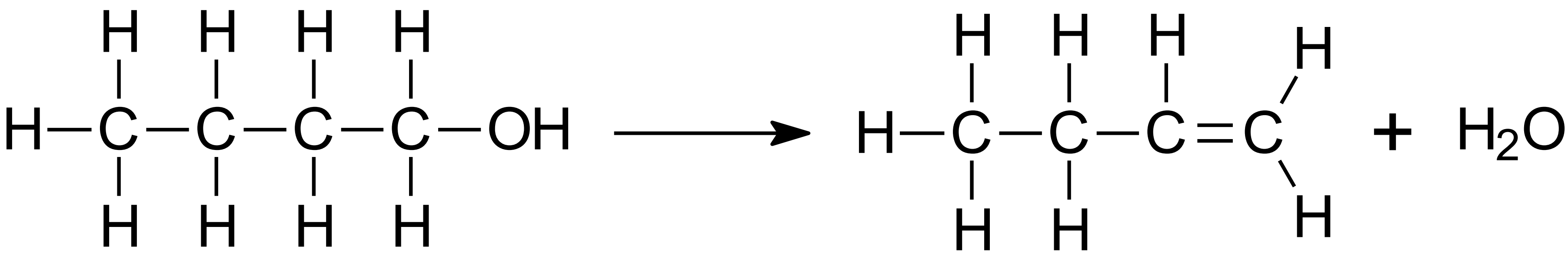
Substitution

1-Chloropropane

Propan-1-ol

Organic Chemistry

Classification of Organic Reactions

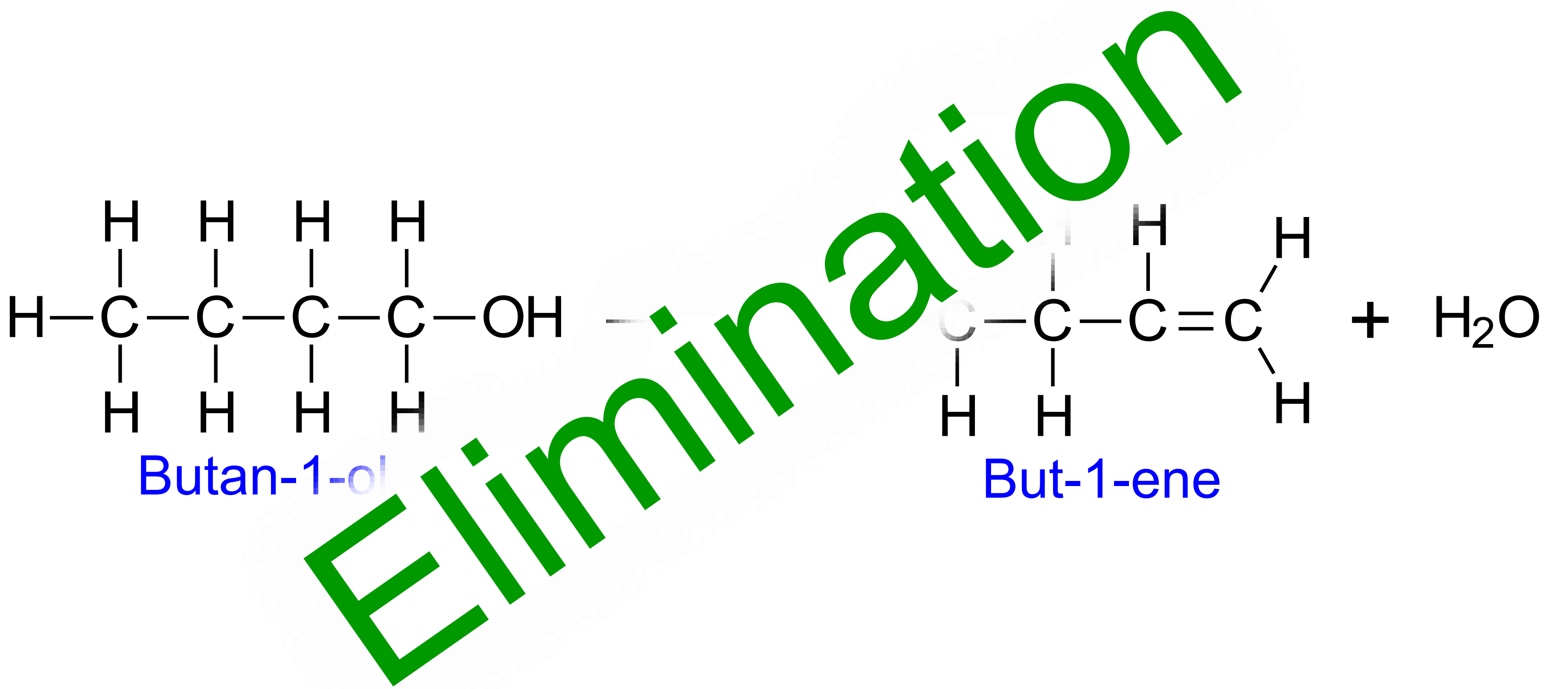


Butan-1-ol

But-1-ene

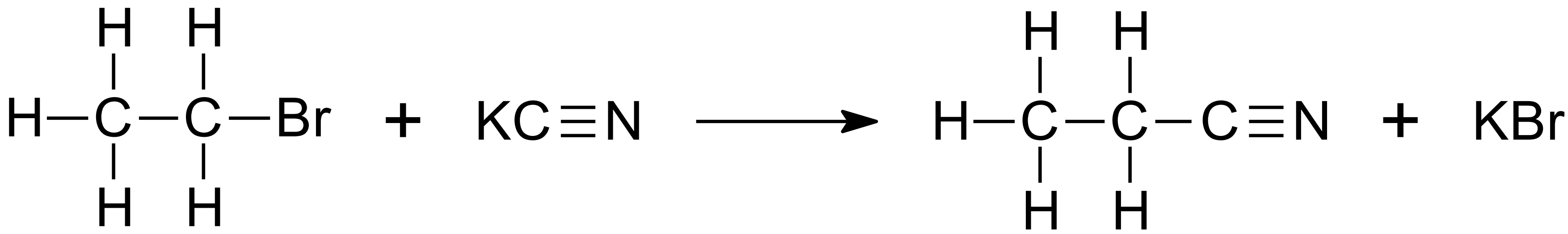
Organic Chemistry

Classification of Organic Reactions



Organic Chemistry

Classification of Organic Reactions



Bromoethane

Propanenitrile

Organic Chemistry

Classification of Organic Reactions

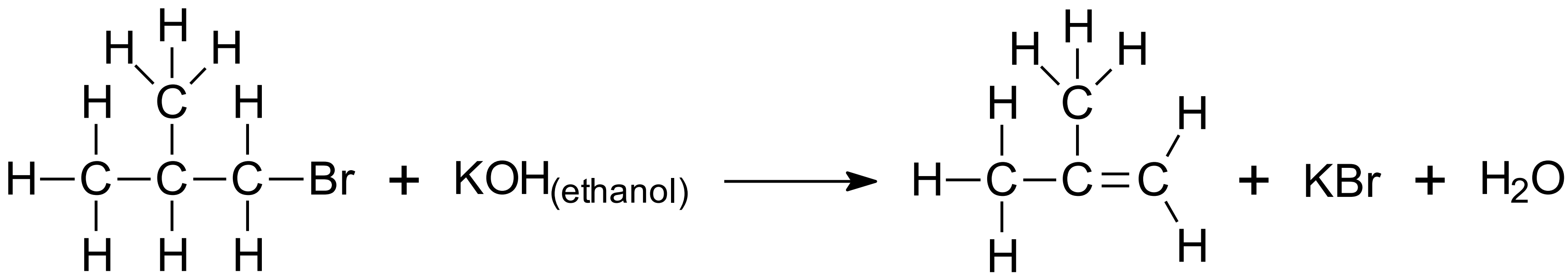
Substitution

Bromoethane

Propanenitrile

Organic Chemistry

Classification of Organic Reactions



1-Bromo-2-methylpropane or 1-Bromo-methylpropane

2-Methylpropene or Methylpropene

Organic Chemistry

Classification of Organic Reactions

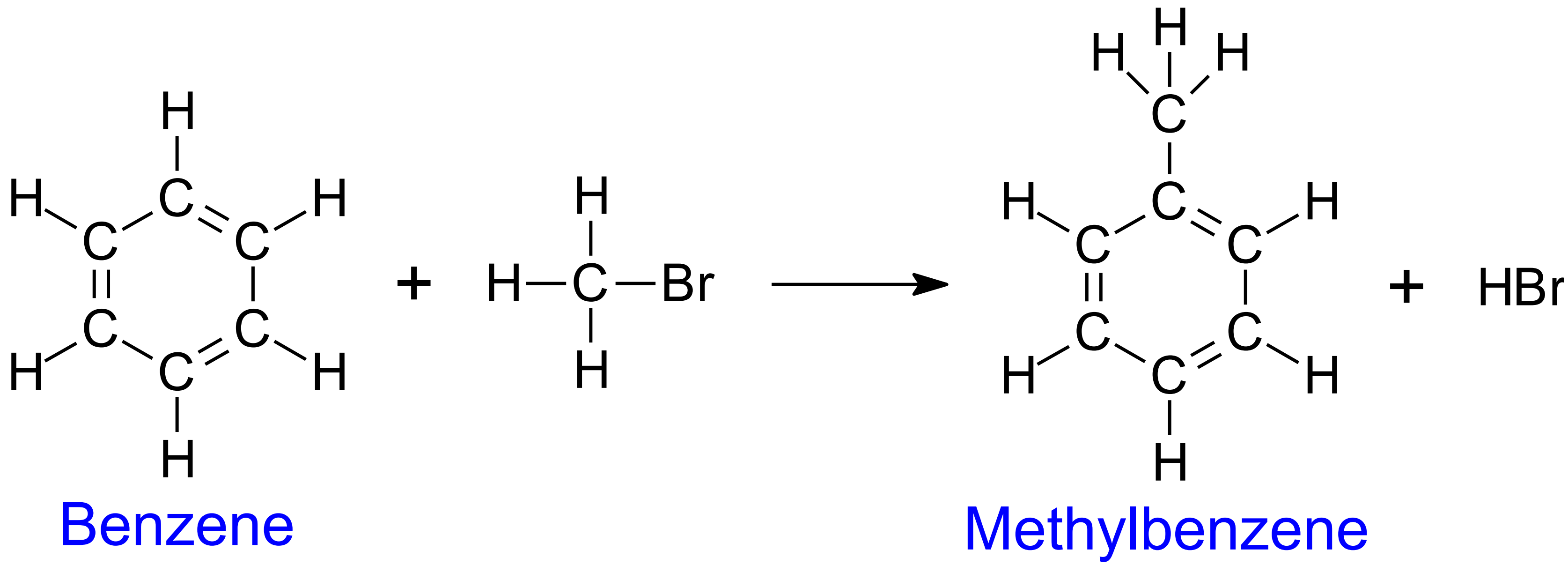
Elimination

1-Bromo-2-methylpropane
or
1-Bromo-methylpropane

2-Methylpropene
or Methylpropene

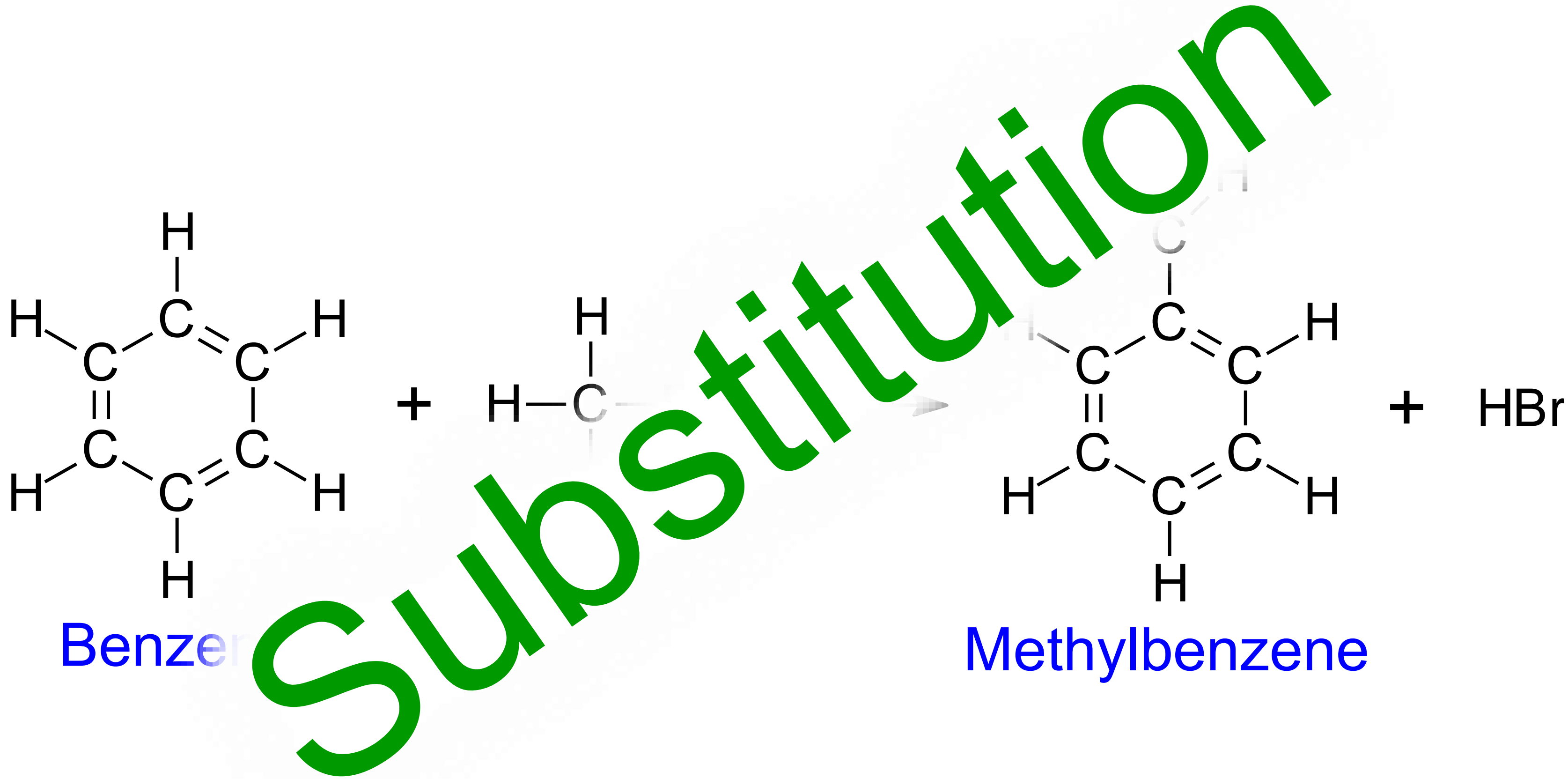
Organic Chemistry

Classification of Organic Reactions



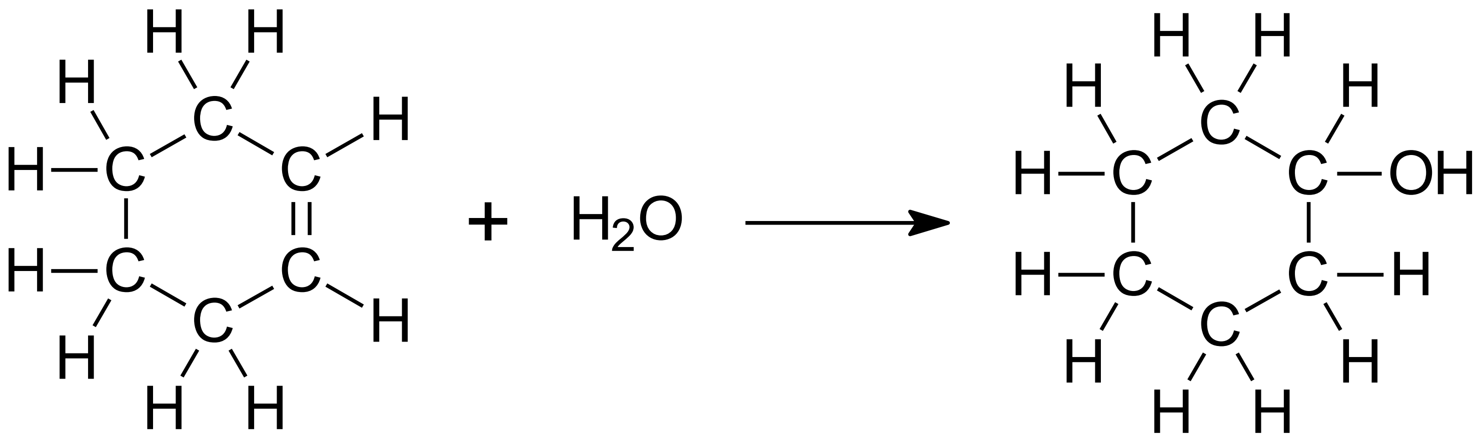
Organic Chemistry

Classification of Organic Reactions



Organic Chemistry

Classification of Organic Reactions



Cyclohexene Cyclohexanol

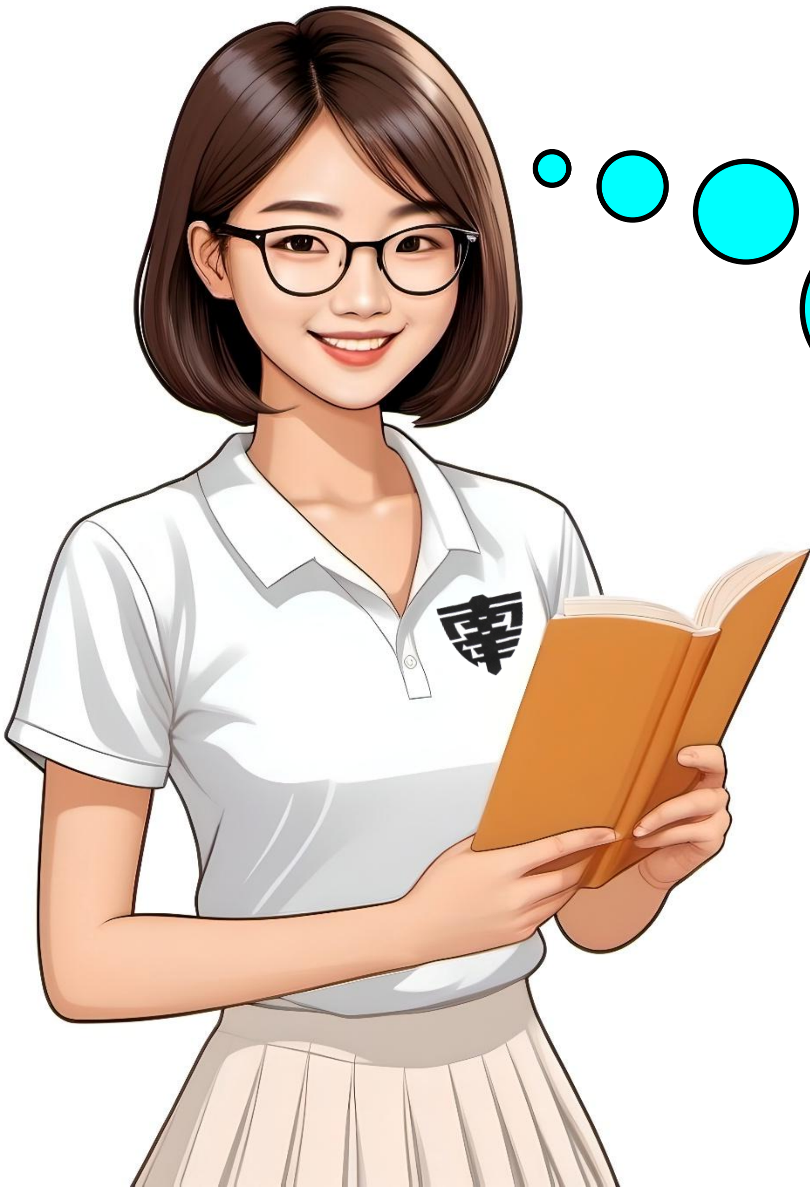
Organic Chemistry

Classification of Organic Reactions

Cyclohexene

Cyclohexanol

Organic Chemistry



What are the *essential reactions* of organic compounds?

- Alkanes
- Halogenoalkanes
- Alkenes
- Alcohols
- Carboxylic Acids

Organic Chemistry

What are the essential reactions of the *alkanes*?

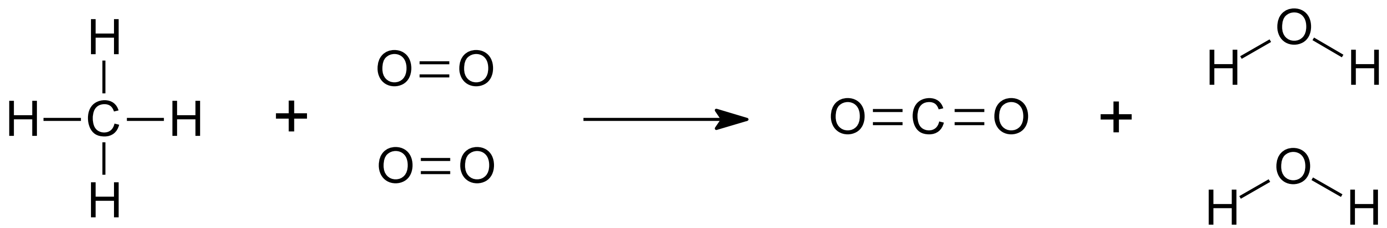
- Combustion
- Substitution
- Cracking

Organic Chemistry

Reactions of the Alkanes – Combustion

The complete combustion of an alkane produces carbon dioxide and water. The reaction is very important because it is highly exothermic.

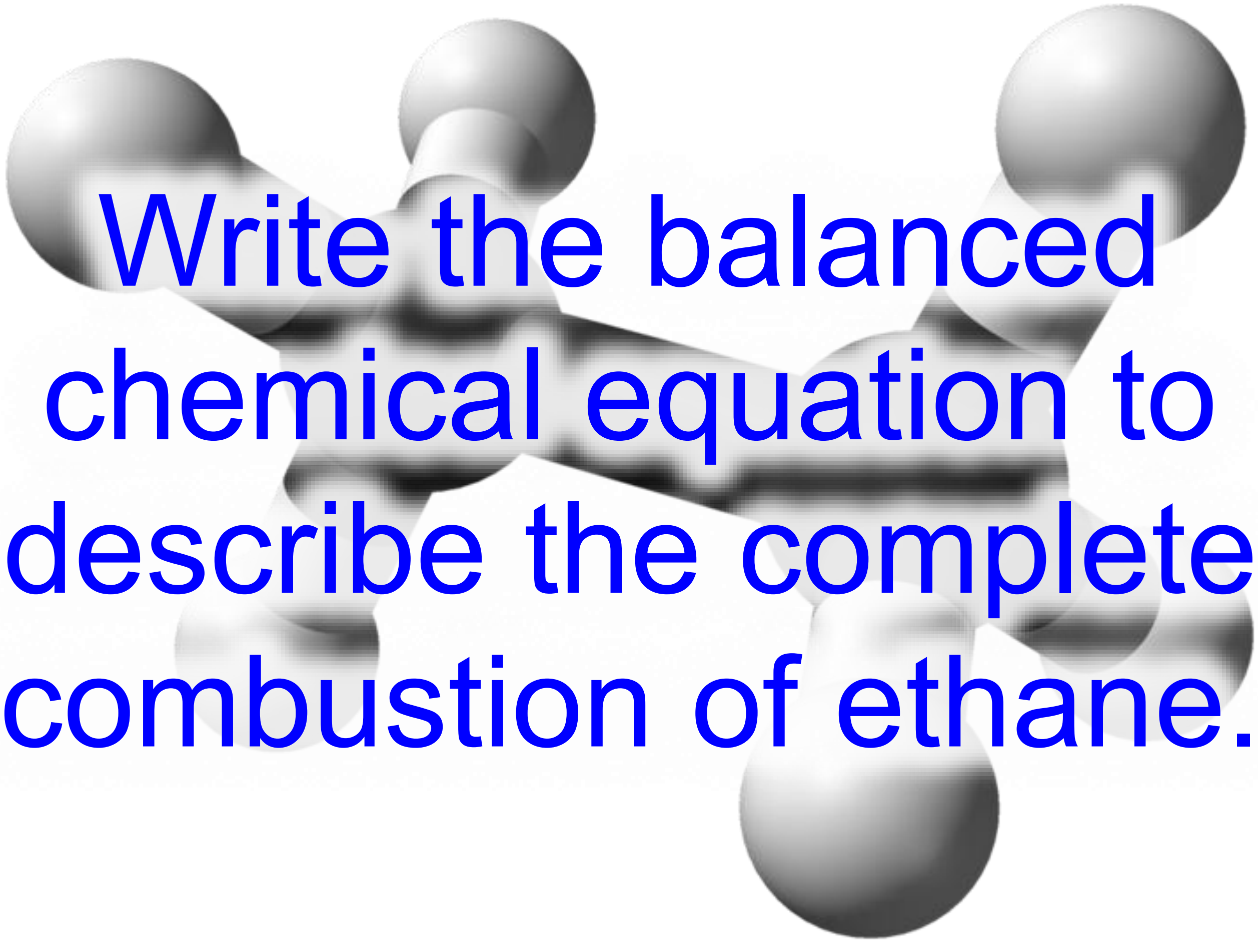
$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$$



Methane Oxygen Carbon Dioxide Water

Organic Chemistry

Reactions of the Alkanes – Combustion

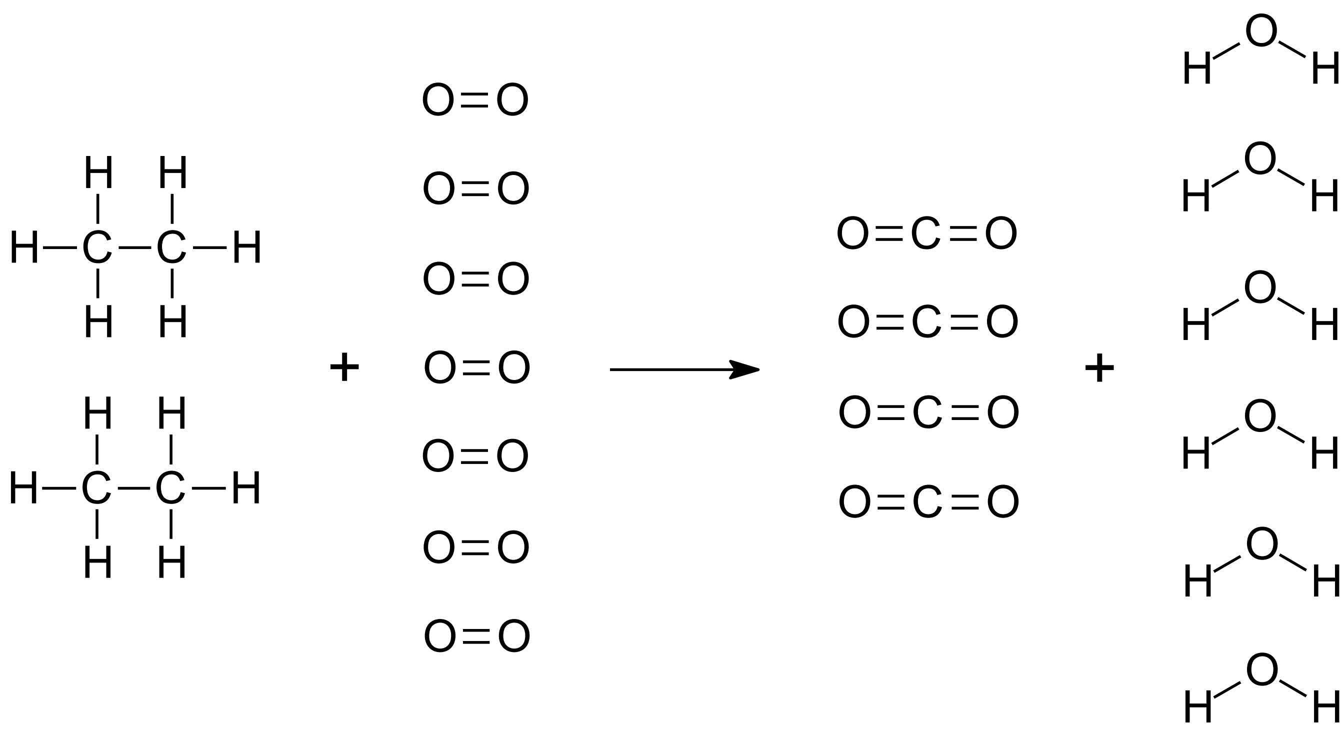


Write the balanced chemical equation to describe the complete combustion of ethane.

Organic Chemistry

Reactions of the Alkanes – Combustion

$$2C_2H_6(g) + 7O_2(g) \rightarrow 4CO_2(g) + 6H_2O(g)$$



Ethane

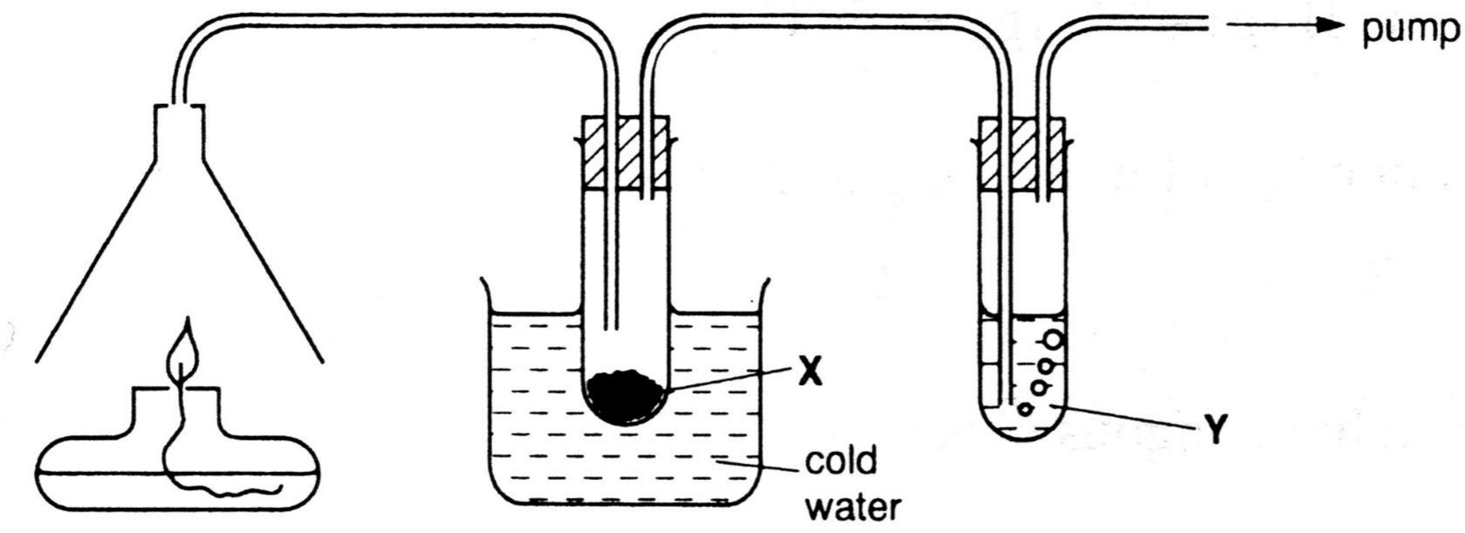
Oxygen

Carbon Dioxide

Water

Organic Chemistry

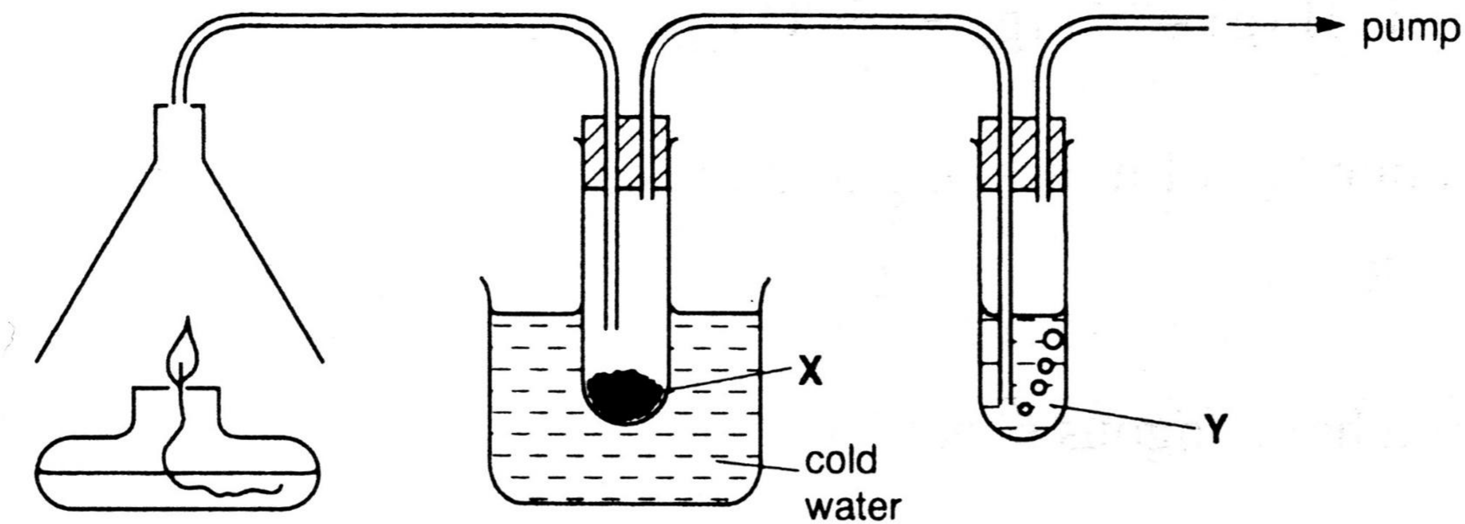
Reactions of the Alkanes – Combustion



- Which chemical, **X**, can be used to detect the presence of *water*? What change would you observe in **X** if water were present?

Organic Chemistry

Reactions of the Alkanes – Combustion



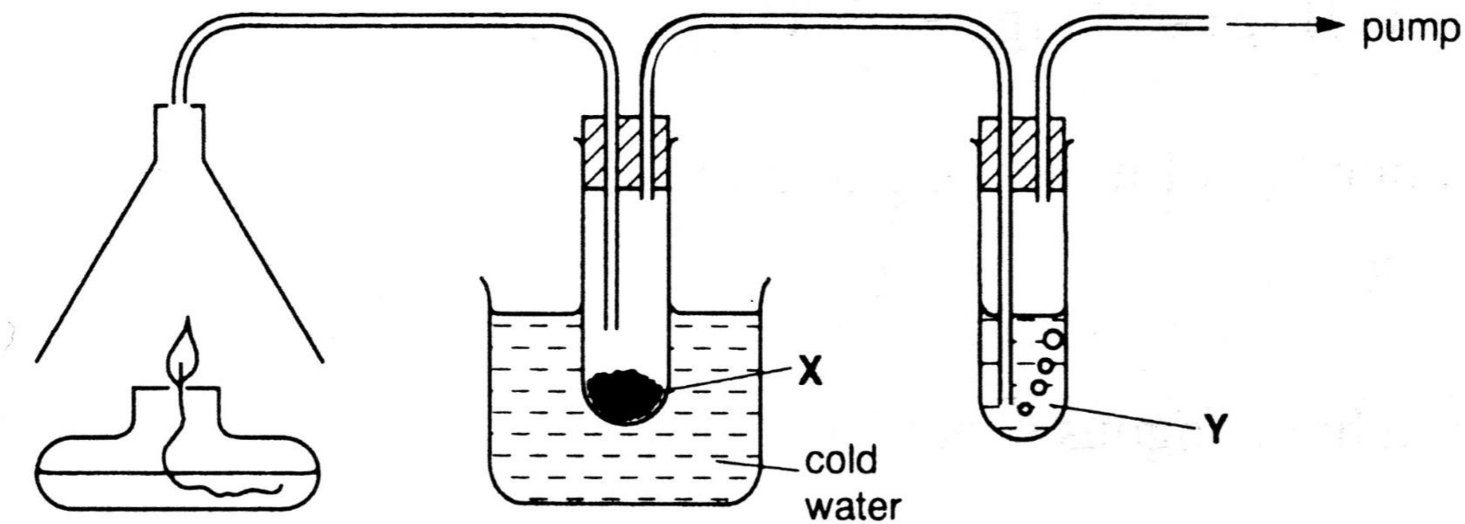
- Which chemical, **X**, can be used to detect the presence of *water*? What change would you observe in **X** if water were present?

- *Anhydrous copper(II) sulfate* can be used to test for water.

The *white anhydrous* copper(II) sulfate will change into *blue hydrated* copper(II) sulfate upon the addition of water.

Organic Chemistry

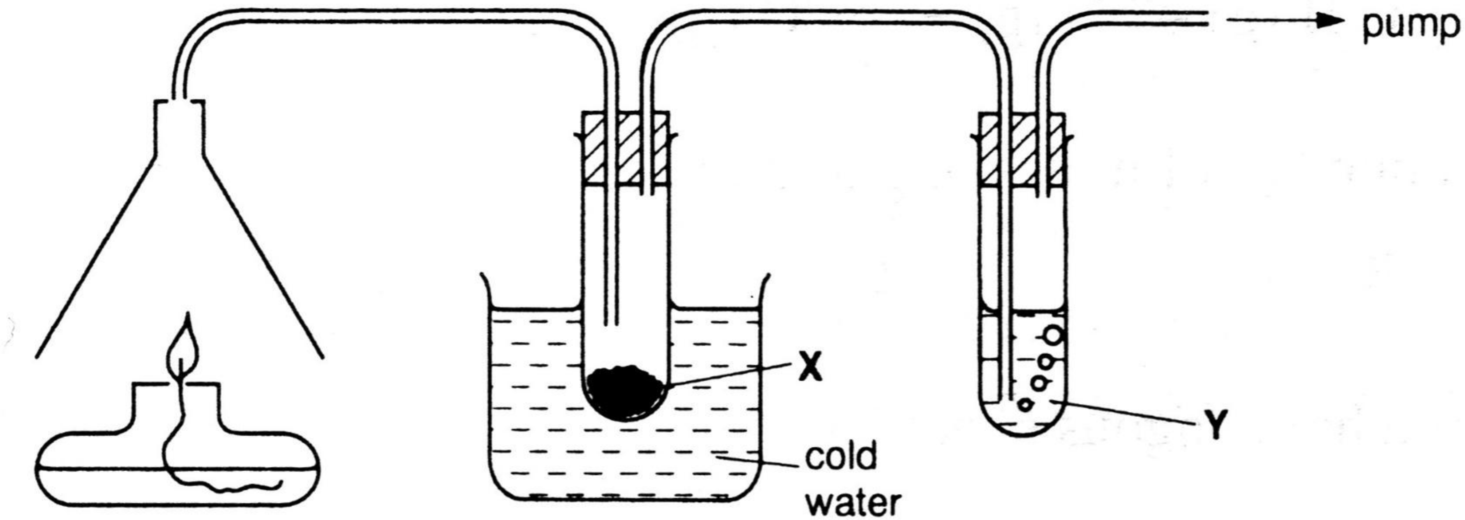
Reactions of the Alkanes – Combustion



- Which chemical, **Y**, can be used to detect the presence of *carbon dioxide*? What change would you observe in **Y** if carbon dioxide were present?

Organic Chemistry

Reactions of the Alkanes – Combustion



- Which chemical, **Y**, can be used to detect the presence of *carbon dioxide*? What change would you observe in **Y** if carbon dioxide were present?

- *Limewater* (an aqueous solution of calcium hydroxide) can be used to test for carbon dioxide. A *white precipitate* will be formed when carbon dioxide is bubbled through limewater.

Organic Chemistry

Reactions of the Alkanes – Combustion

- In a *limited* supply of oxygen, where the alkane is in excess, *incomplete combustion* of the hydrocarbon will take place.

- Incomplete combustion of a hydrocarbon can produce a range of products, including *carbon monoxide* (a toxic gas that irreversibly binds to haemoglobin), *soot* (fine particles of carbon) and *water*.

propane + oxygen → carbon monoxide + soot + water

$$C_3H_8(g) + 3O_2(g) \rightarrow 2CO(g) + C(s) + 4H_2O(g)$$

Organic Chemistry

Reactions of the Alkanes – Combustion

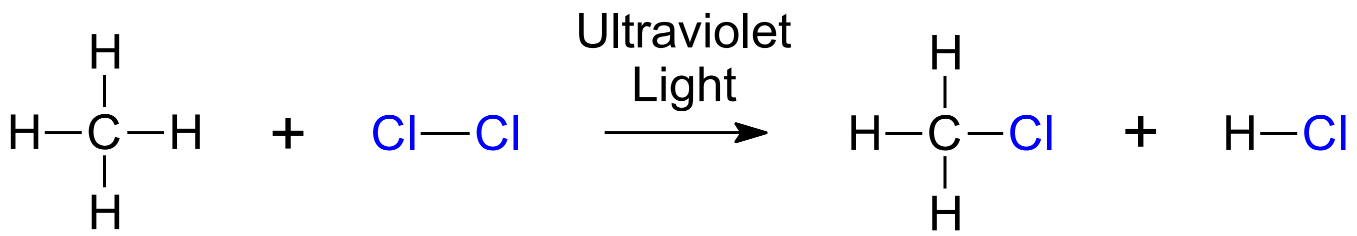
- Incomplete combustion: Luminous flame.
- Particles of soot glow in the hot flame.
- Relatively cooler flame.

- Complete combustion: Non-luminous flame.
- Products are CO_2 and H_2O.
- Relatively hotter flame.

Organic Chemistry

Reactions of the Alkanes – Substitution into Methane, CH_4

The hydrogen of an alkane can be substituted by a Group 17 element in the presence of *ultraviolet light*. The reaction is a *free radicle reaction*, producing a complex mixture of products.



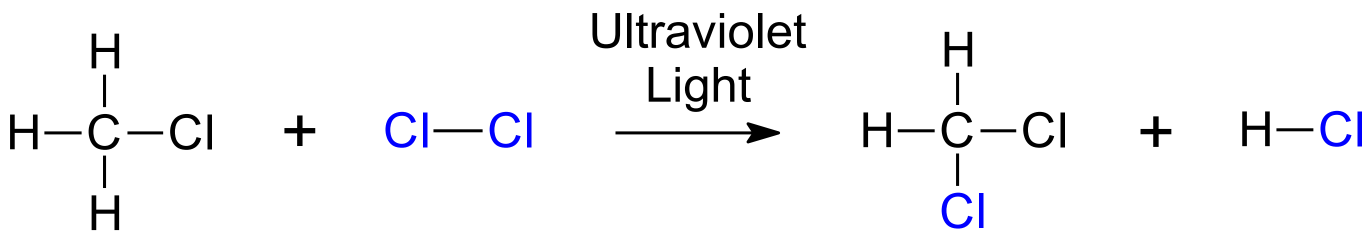
Methane

Chloromethane

Organic Chemistry

Reactions of the Alkanes – Substitution into Methane, CH_4

The hydrogen of an alkane can be substituted by a Group 17 element in the presence of *ultraviolet light*. The reaction is a *free radicle reaction*, producing a complex mixture of products.

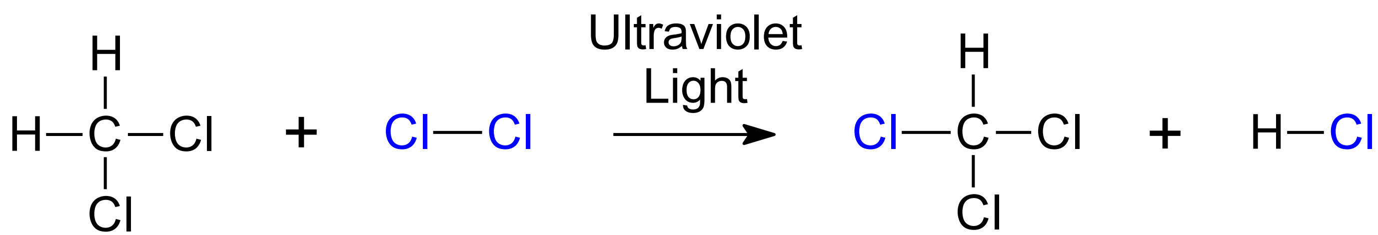


Chloromethane Dichloromethane

Organic Chemistry

Reactions of the Alkanes – Substitution into Methane, CH_4

The hydrogen of an alkane can be substituted by a Group 17 element in the presence of *ultraviolet light*. The reaction is a *free radical reaction*, producing a complex mixture of products.



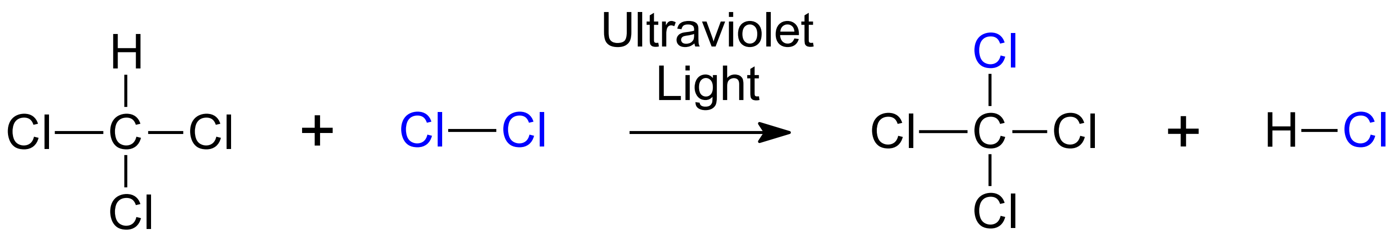
Dichloromethane

Trichloromethane

Organic Chemistry

Reactions of the Alkanes – Substitution into Methane, CH_4

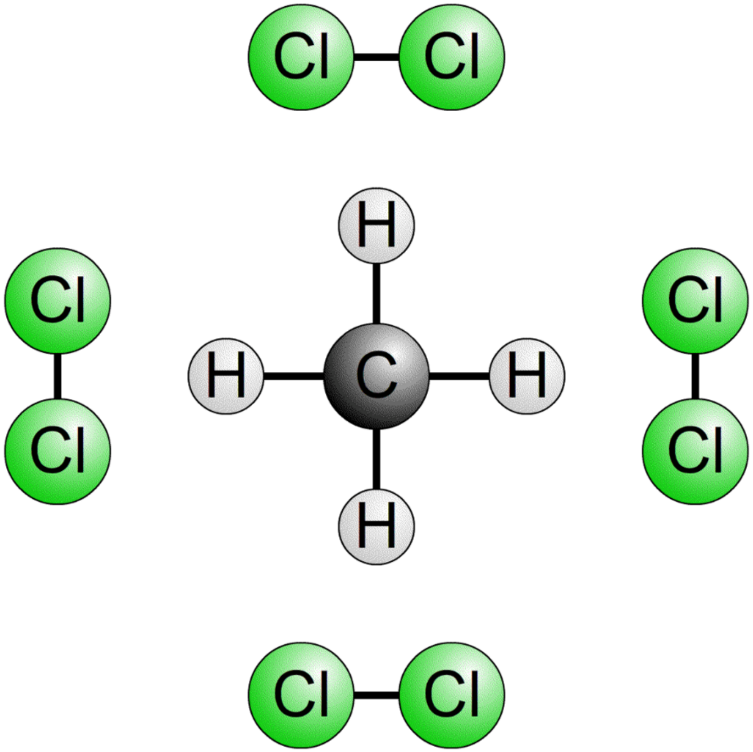
The hydrogen of an alkane can be substituted by a Group 17 element in the presence of *ultraviolet light*. The reaction is a *free radical reaction*, producing a complex mixture of products.



Trichloromethane Tetrachloromethane

Organic Chemistry

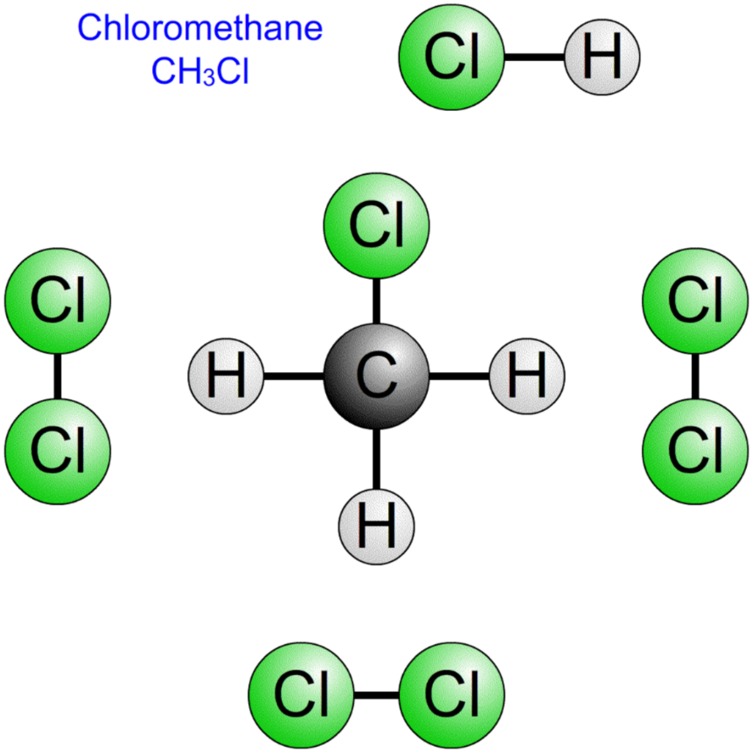
Reactions of the Alkanes – Substitution into Methane, CH_4



- Energy contained within the *ultraviolet light* is used to break C*l* – C*l* covalent bonds.

Organic Chemistry

Reactions of the Alkanes – Substitution into Methane, CH_4



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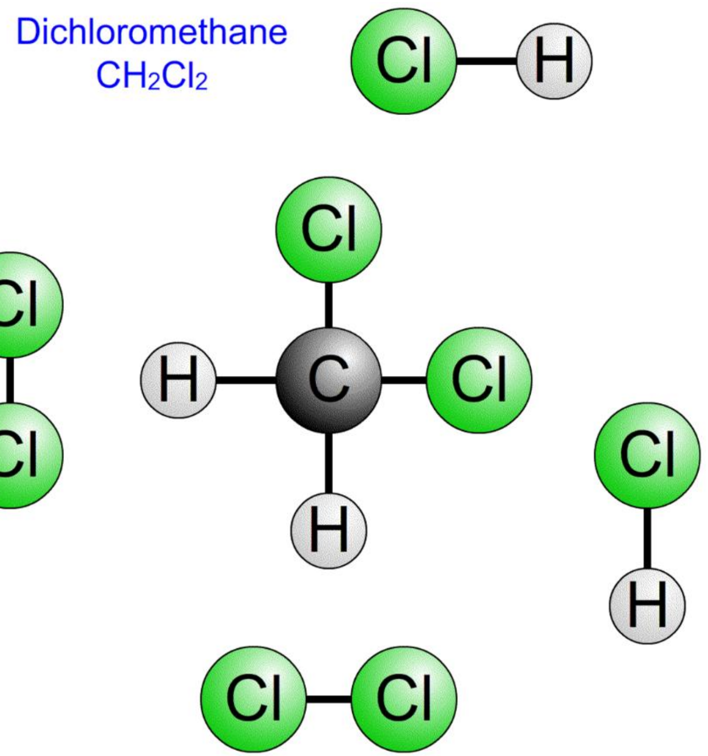
Organic Chemistry

Reactions of the Alkanes – Substitution into Methane, CH_4



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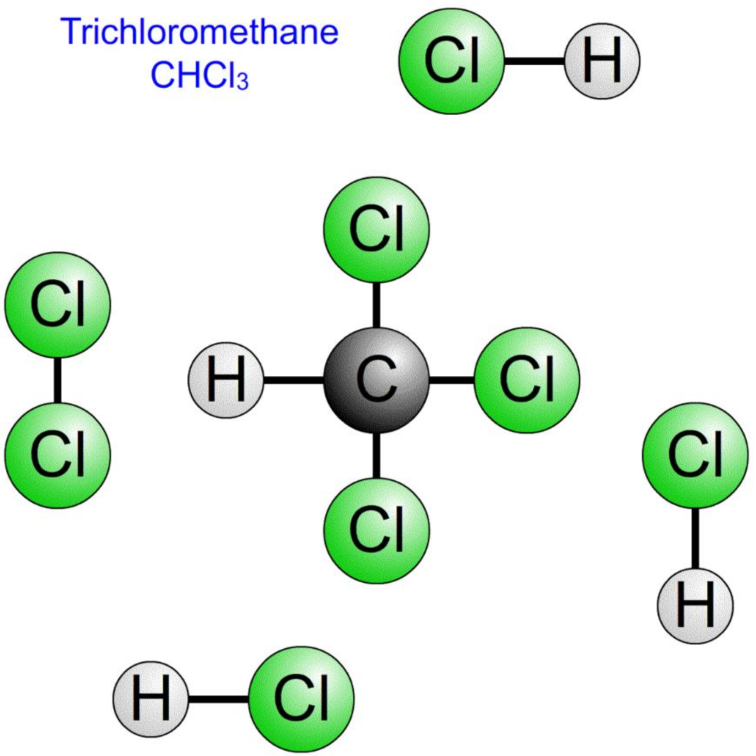
Organic Chemistry

Reactions of the Alkanes – Substitution into Methane, CH_4



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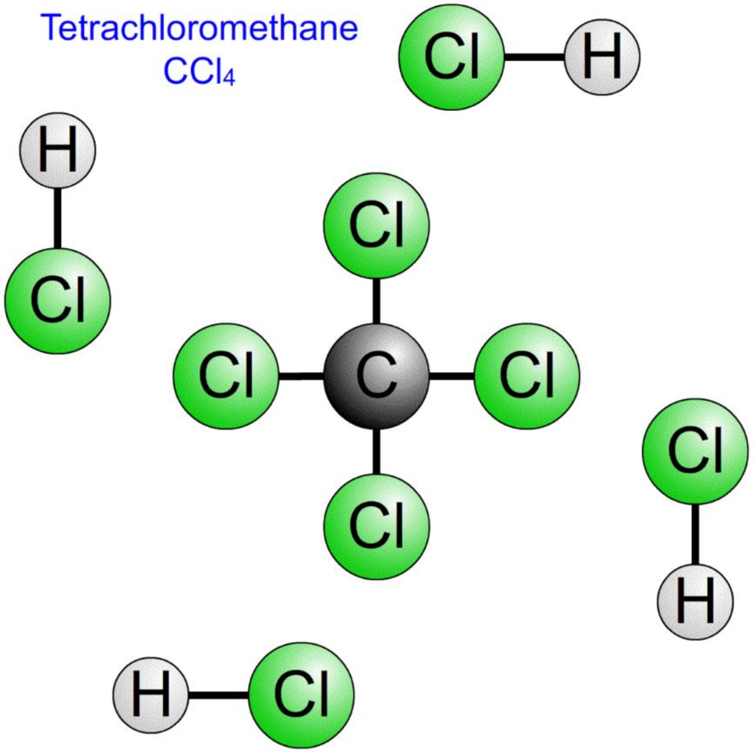
Organic Chemistry

Reactions of the Alkanes – Substitution into Methane, CH_4



- Energy contained within the *ultraviolet light* is used to break C*l* – C*l* covalent bonds.

Organic Chemistry

Reactions of the Alkanes – Substitution into Methane, CH_4

- Ultraviolet light provides the *activation energy* necessary to break the covalent bond between the two chlorine atoms in a molecule of chlorine.

- Two chlorine *radicals* are formed. These are highly reactive species due to their single unpaired electrons.

chlorine molecule → chlorine radical + chlorine radical

$$Cl\text{–}Cl \rightarrow Cl\cdot + Cl\cdot$$

methane molecule + chlorine radical → methyl radical + hydrogen chloride

$$CH_4 + Cl\cdot \rightarrow CH_3\cdot + H\text{–}Cl$$

methyl radical + chlorine molecule → chloromethane + chlorine radical

$$CH_3\cdot + Cl\text{–}Cl \rightarrow CH_3Cl + Cl\cdot$$

Organic Chemistry

Reactions of the Alkanes – Substitution into Methane, CH_4

- Ultraviolet light provides the *activation energy* necessary to break the covalent bond between the two chlorine atoms in a molecule of chlorine.

- Two chlorine *radicals* are formed. These are highly reactive species due to their single unpaired electrons.

chlorine molecule → chlorine radical + chlorine radical

$$Cl–Cl \rightarrow Cl\cdot + Cl\cdot$$

methane molecule + chlorine radical → methyl radical + hydrogen chloride

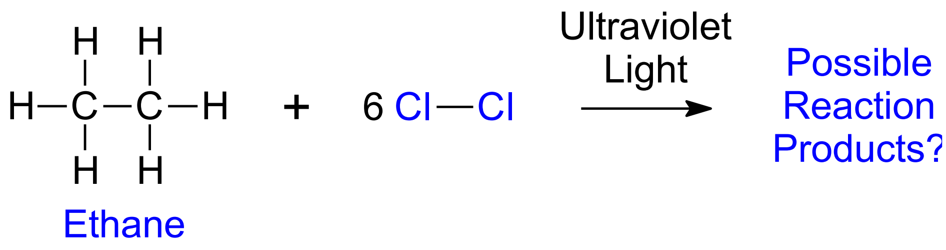
$$CH_4 + Cl\cdot \rightarrow CH_3\cdot + H–Cl$$

methyl radical + chlorine molecule → chloromethane + chlorine radical

$$CH_3\cdot + Cl–Cl \rightarrow CH_3Cl + Cl\cdot$$

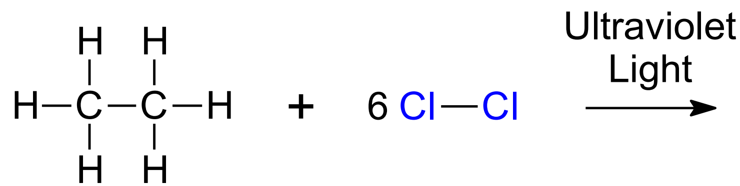
Organic Chemistry

Reactions of the Alkanes – Substitution into Ethane, C_2H_6



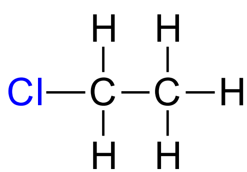
Organic Chemistry

Reactions of the Alkanes – Substitution into Ethane, C_2H_6

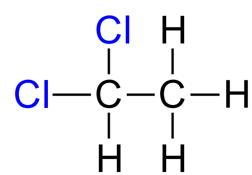


Ethane

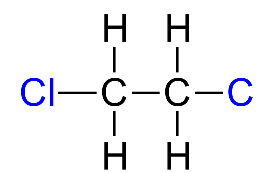
Possible Reaction Products?



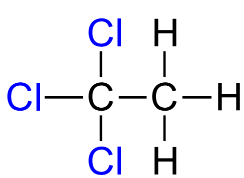
1-Chloroethane
(or just Chloroethane)



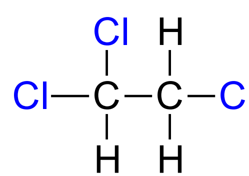
1,1-Dichloroethane



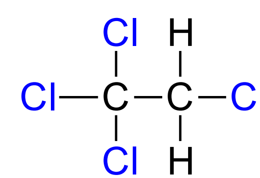
1,2-Dichloroethane



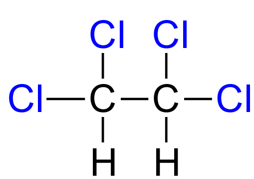
1,1,1-Trichloroethane



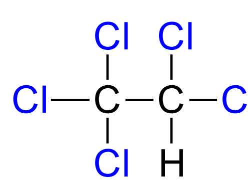
1,1,2-Trichloroethane



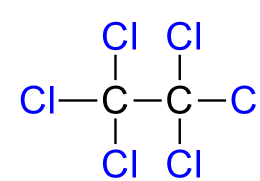
1,1,1,2-Tetrachloroethane



1,1,2,2-Tetrachloroethane



1,1,1,2,2-Pentachloroethane
(or just Pentachloroethane)

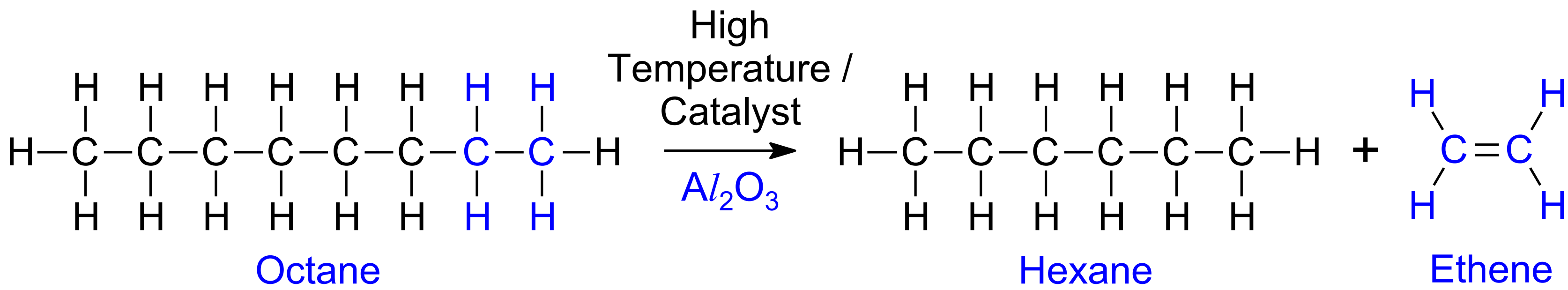


1,1,1,2,2,2-Hexachloroethane
(or just Hexachloroethane)

Organic Chemistry

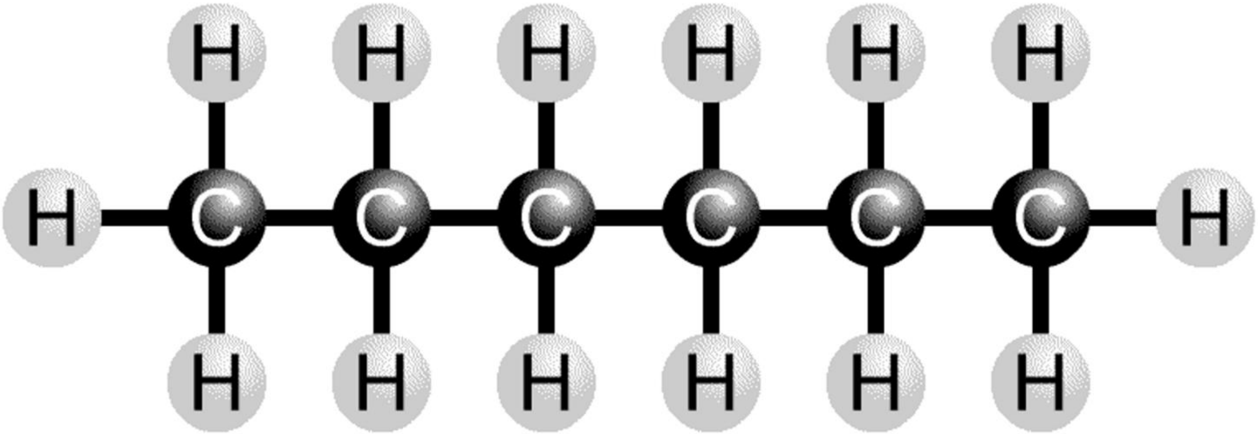
Reactions of the Alkanes – Cracking

The catalytic cracking of long-chain alkanes produces short-chain alkanes and alkenes as reaction products. Short-chain alkanes tend to be more useful than long-chain alkanes, and alkenes can be used in organic synthesis.



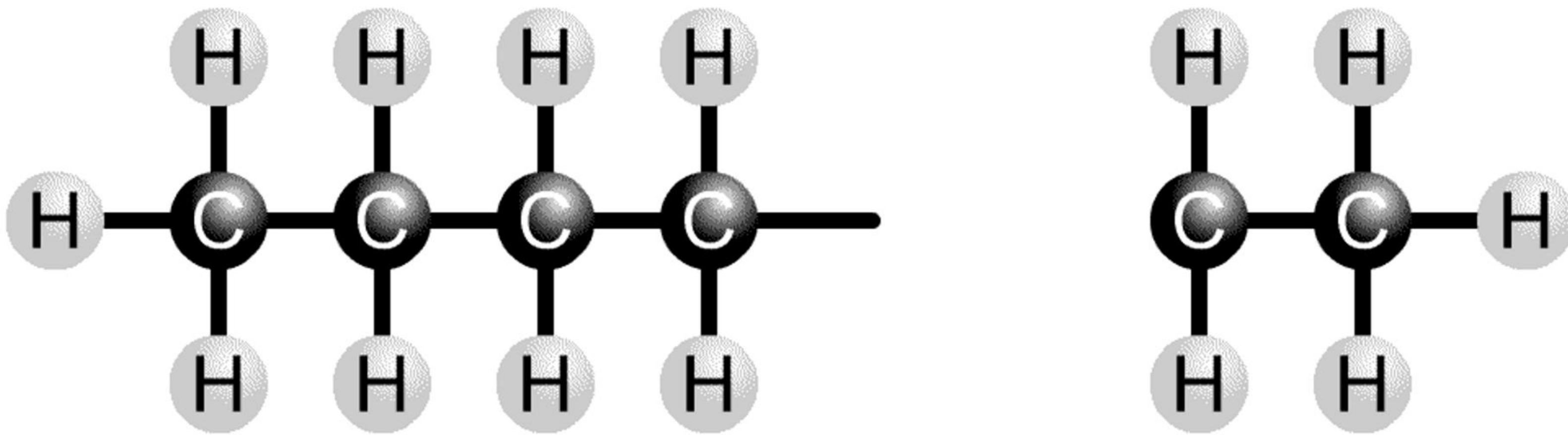
Organic Chemistry

Reactions of the Alkanes – Cracking



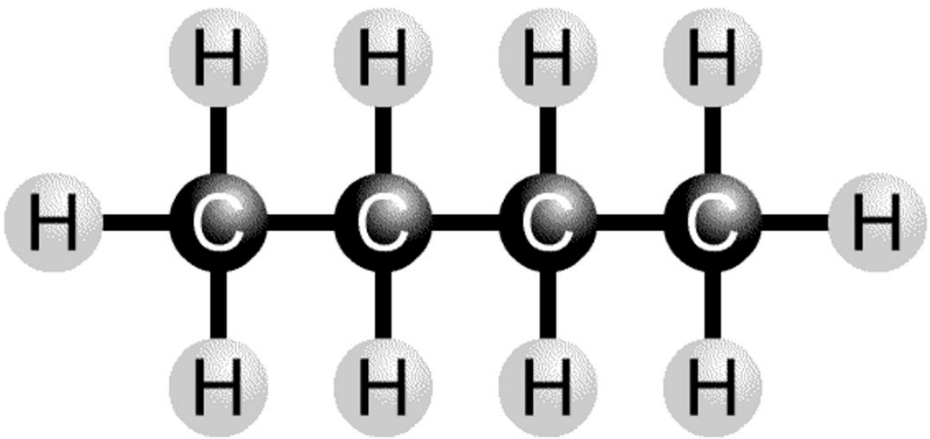
Organic Chemistry

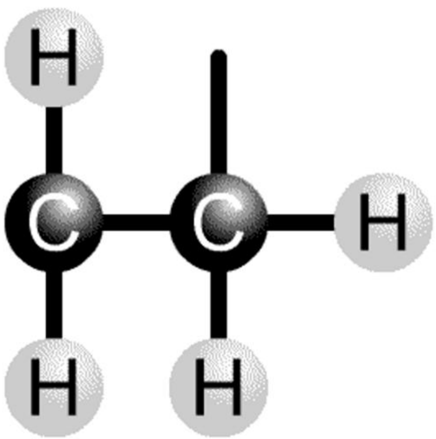
Reactions of the Alkanes – Cracking



Organic Chemistry

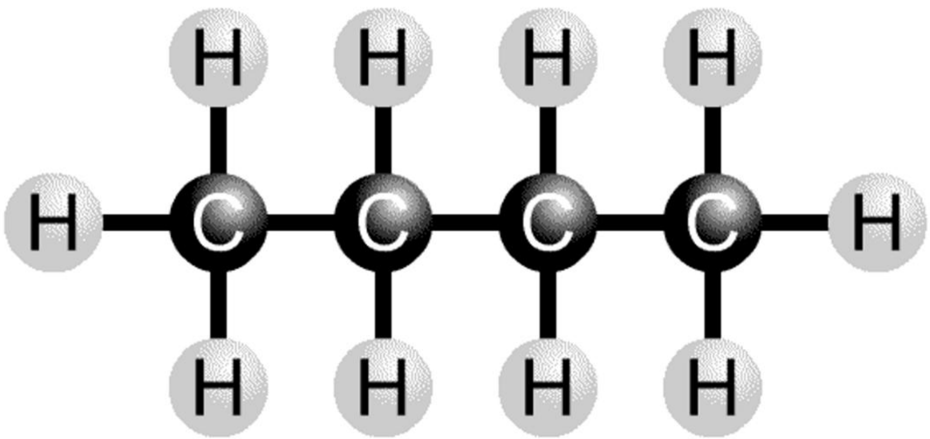
Reactions of the Alkanes – Cracking

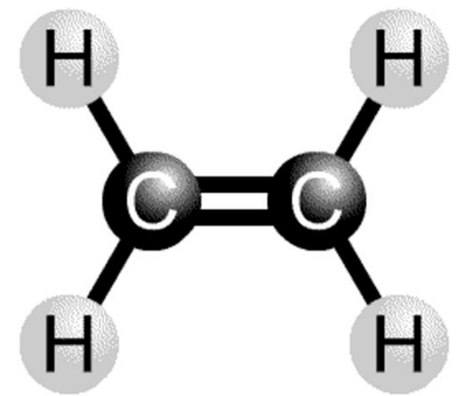




Organic Chemistry

Reactions of the Alkanes – Cracking





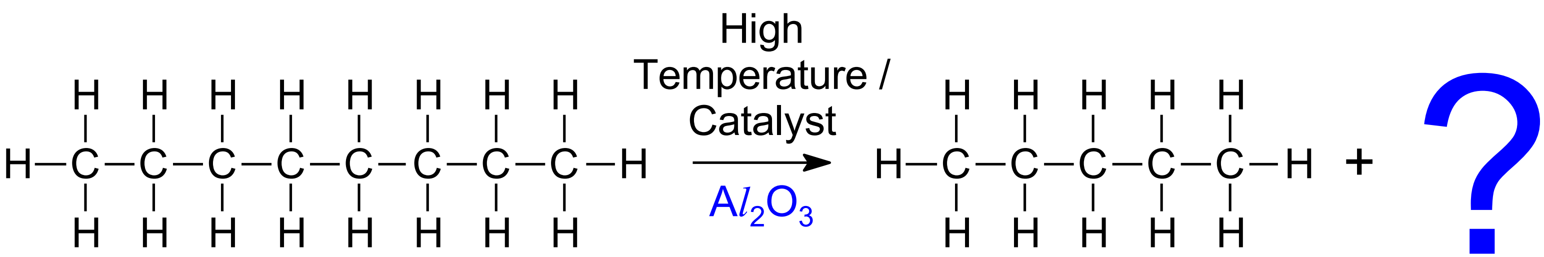
long chain alk*ane* → short chain alk*ane* + short chain alk*ene*

hexane → butane + ethene

$C_6H_{14} \rightarrow C_4H_{10} + C_2H_4$

Organic Chemistry

Reactions of the Alkanes – Cracking

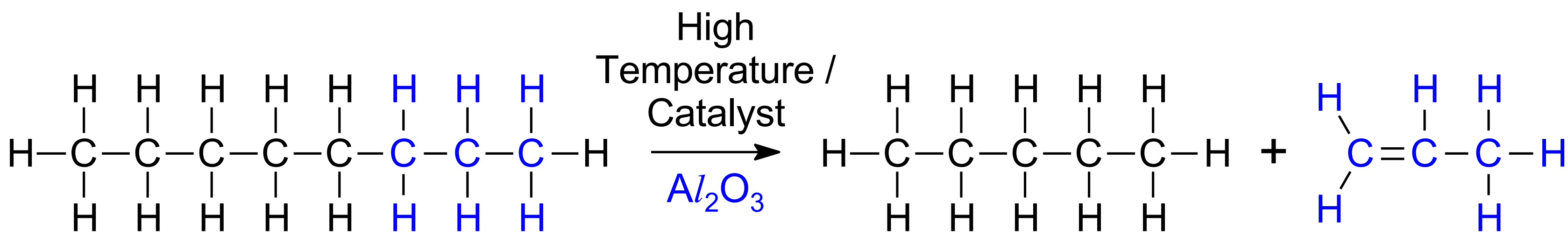


Octane

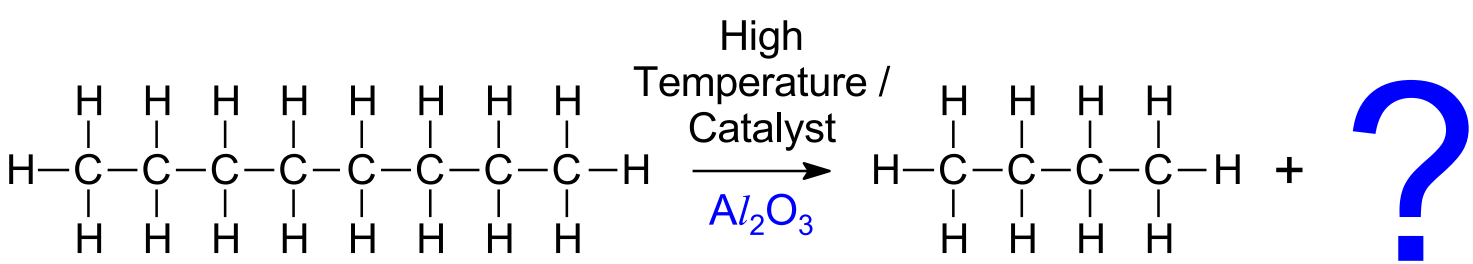
Pentane

Organic Chemistry

Reactions of the Alkanes – Cracking



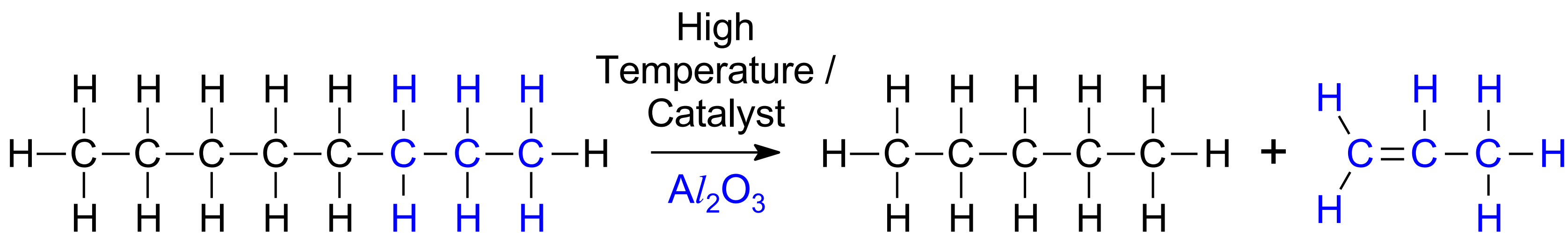
Octane Pentane Propene



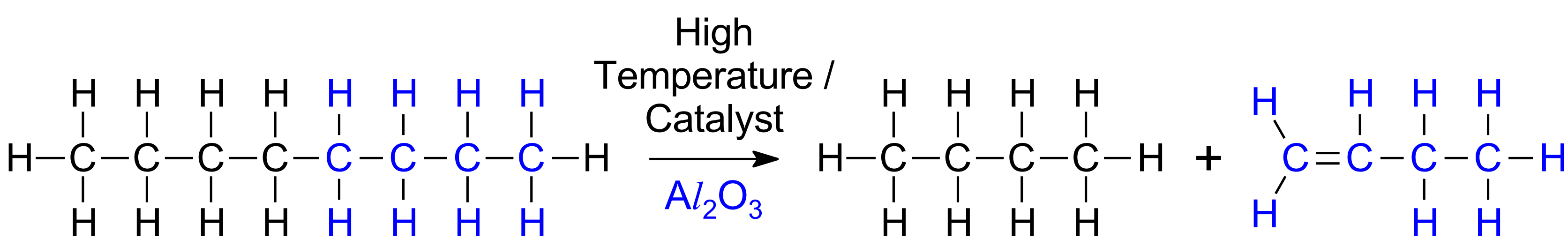
Octane Butane

Organic Chemistry

Reactions of the Alkanes – Cracking



Octane → Pentane + Propene



Octane → Butane + But-1-ene

Organic Chemistry

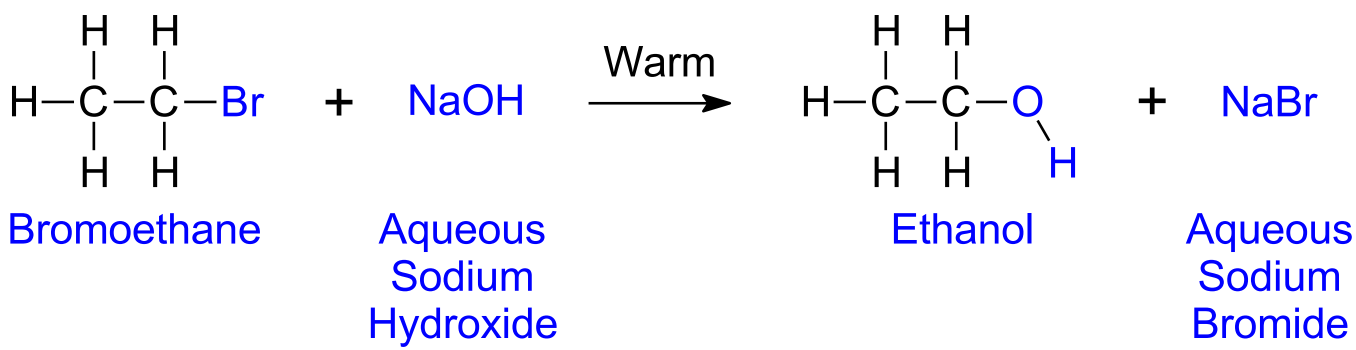
What are the essential reactions of the *halogenoalkanes*?

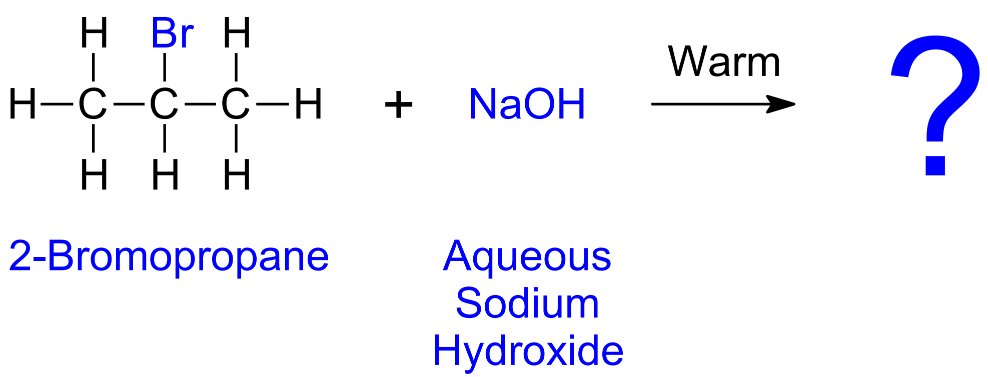
- Substitution

Organic Chemistry

Reactions of the Halogenoalkanes – Substitution

Warming a halogenoalkane with an aqueous solution of sodium hydroxide forms an alcohol as the main reaction product. This is an example of a substitution reaction.





Organic Chemistry

Reactions of the Halogenoalkanes – Substitution

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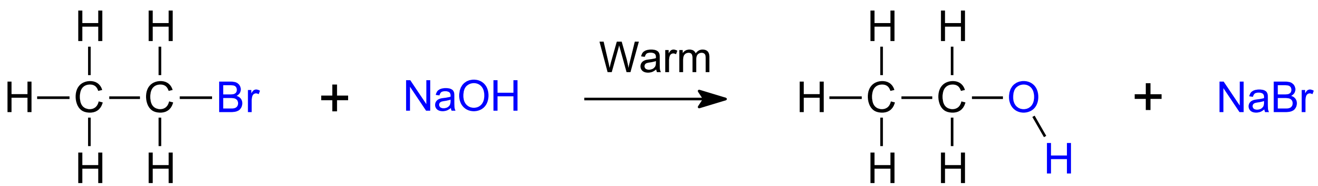
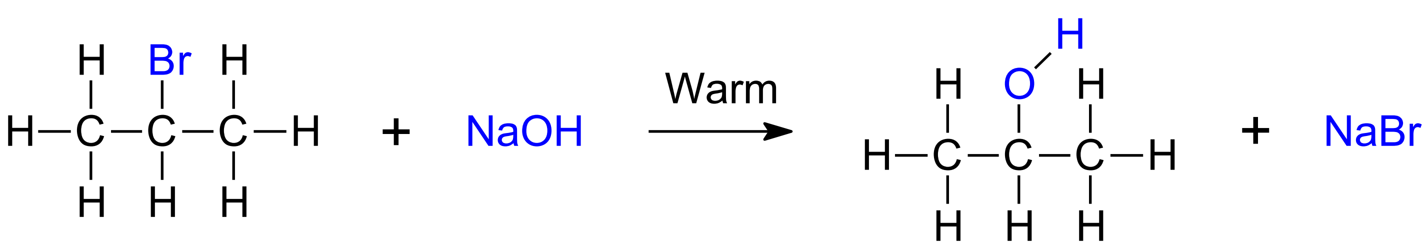
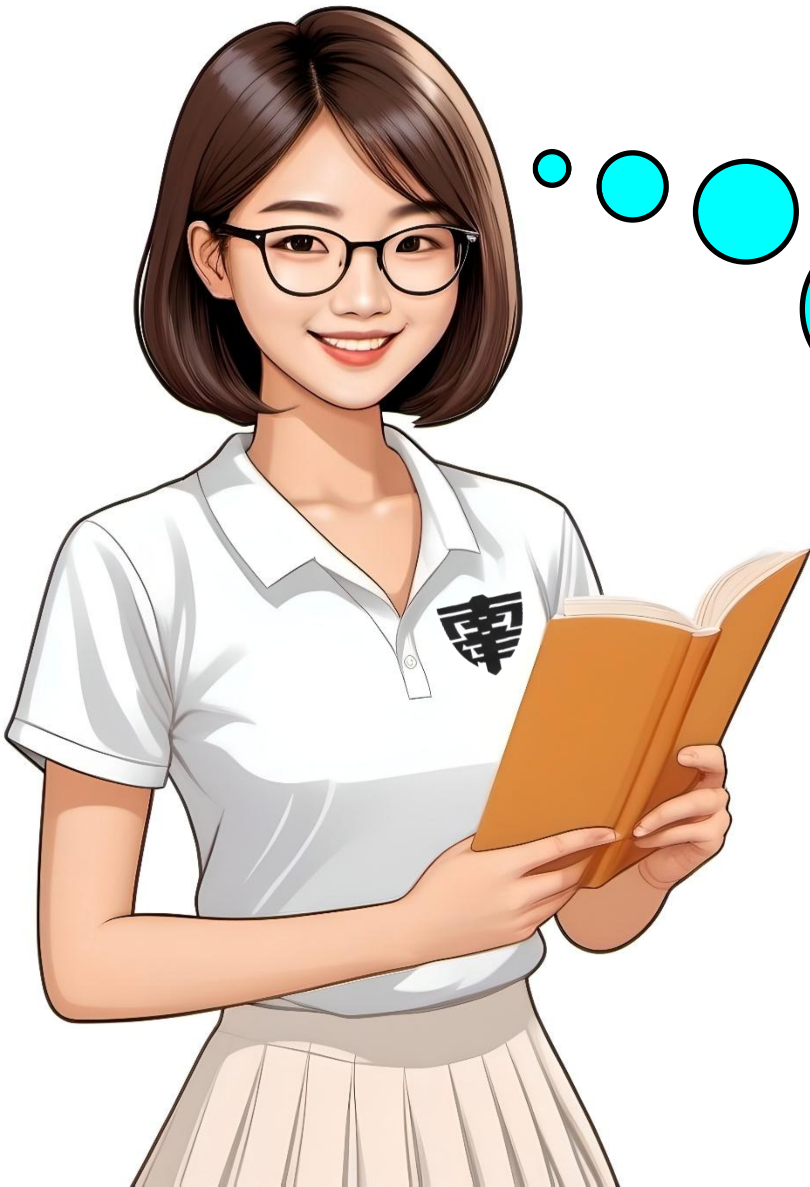


Bromoethane — Aqueous Sodium Hydroxide — Ethanol — Aqueous Sodium Bromide



2-Bromopropane — Aqueous Sodium Hydroxide — Propan-2-ol — Aqueous Sodium Bromide

Organic Chemistry



What are the essential reactions of the *alkenes*?

- Combustion
- Addition

Organic Chemistry

Reactions of the Alkenes – Combustion

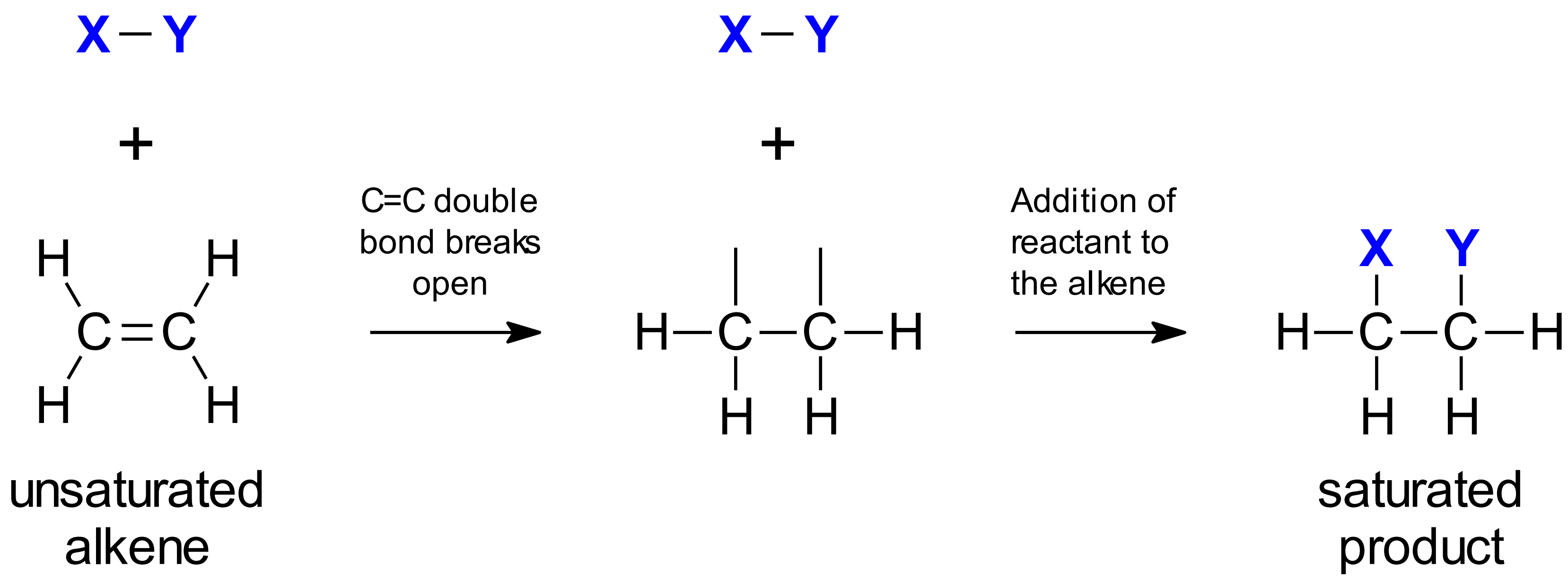
- Alkenes tend to undergo *incomplete combustion*, producing *luminous* (orange / yellow) *sooty flames*.
- Luminous, sooty flames are evidence that the organic compound undergoing combustion is *unsaturated*.
- Unsaturated organic compounds undergo incomplete combustion because they contain a relatively *high percentage carbon*. Compare saturated with unsaturated:

→ Percentage carbon in *butane* $CH_3CH_2CH_2CH_3$:
$[(4 \times 12) \div ((4 \times 12) + 10)] \times 100 = 82.8\%$

→ Percentage carbon in *buta-1,3-diene* $CH_2=CHCH=CH_2$:
$[(4 \times 12) \div ((4 \times 12) + 6)] \times 100 = 88.9\%$

Organic Chemistry

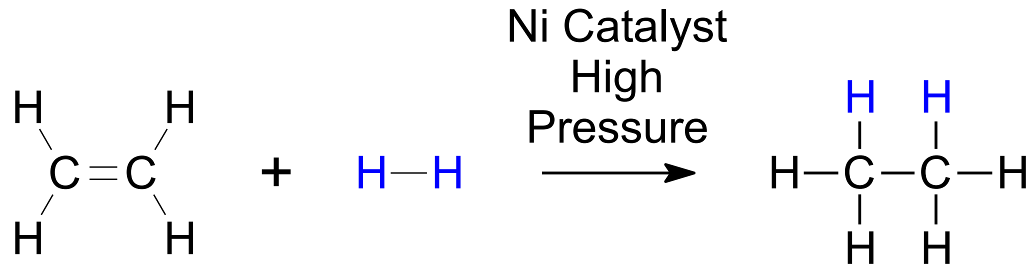
Reactions of the Alkenes – Addition



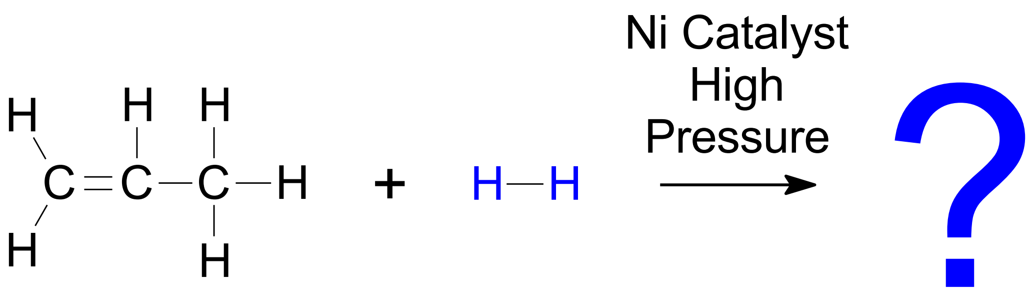
Organic Chemistry

Reactions of the Alkenes – Addition

Alkenes (unsaturated hydrocarbons) react with hydrogen in the presence of a nickel catalyst to form an alkane. This is an example of an addition reaction.



Ethene Hydrogen Ethane



Propene Hydrogen

Organic Chemistry

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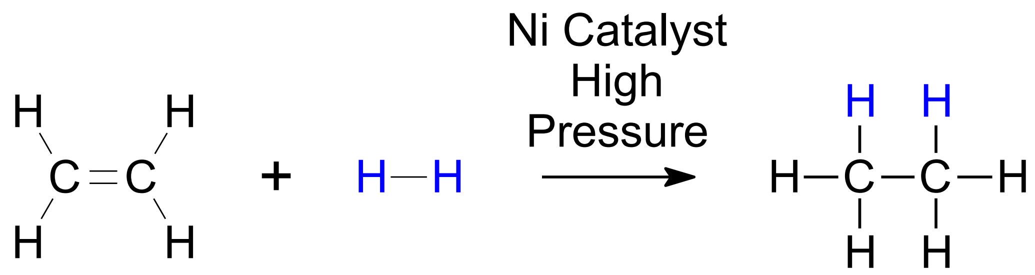
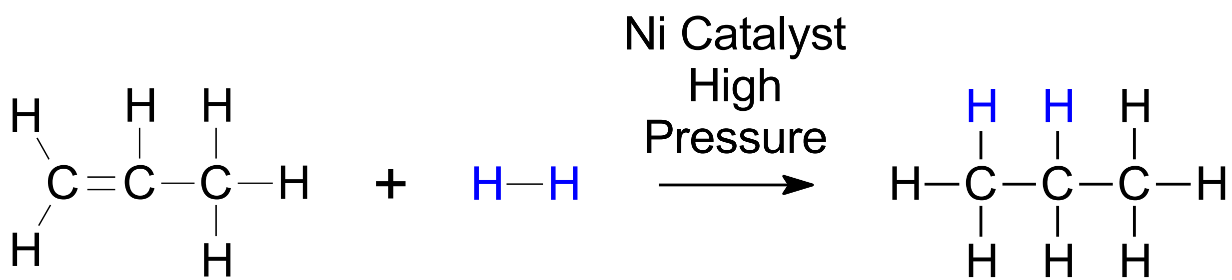


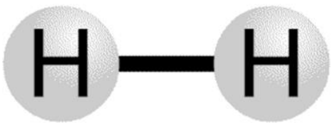
Ethene Hydrogen Ethane



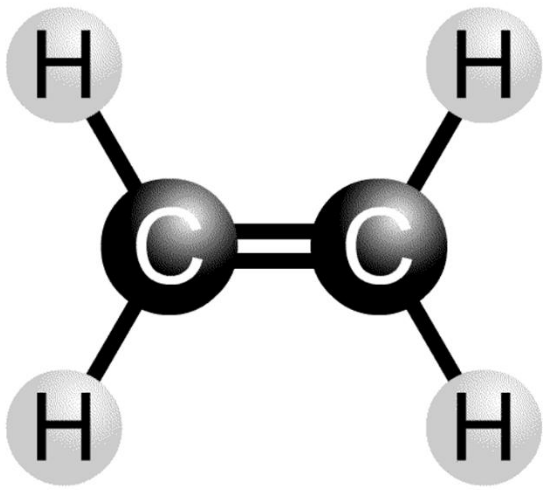
Propene Hydrogen Propane

Organic Chemistry

Reactions of the Alkenes – Addition



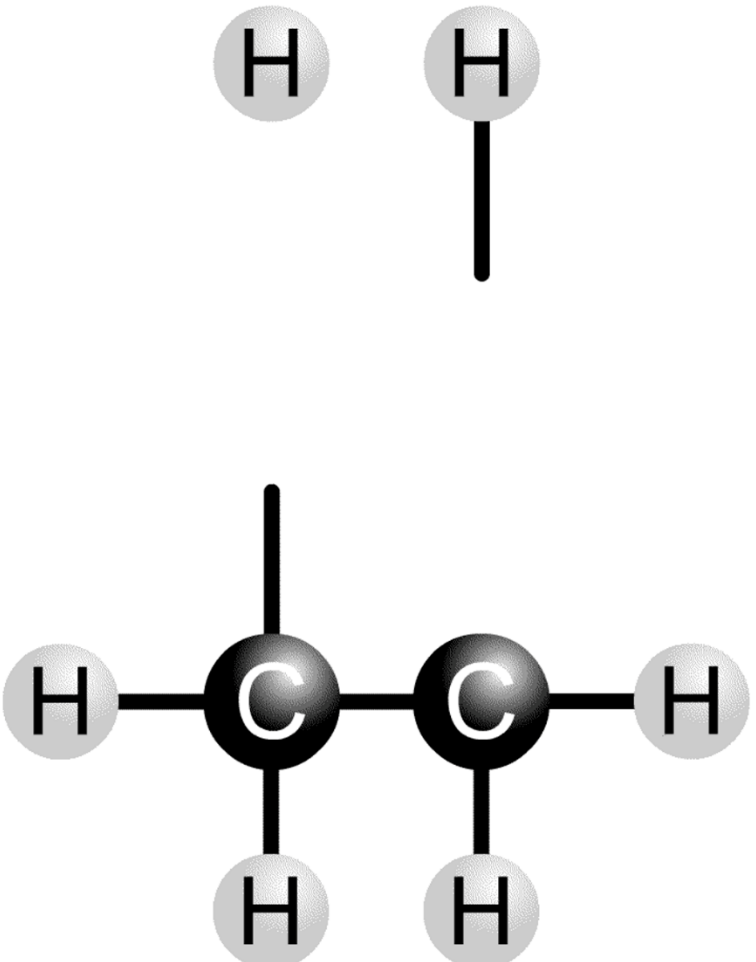
nickel catalyst and high pressure



Organic Chemistry

Reactions of the Alkenes – Addition

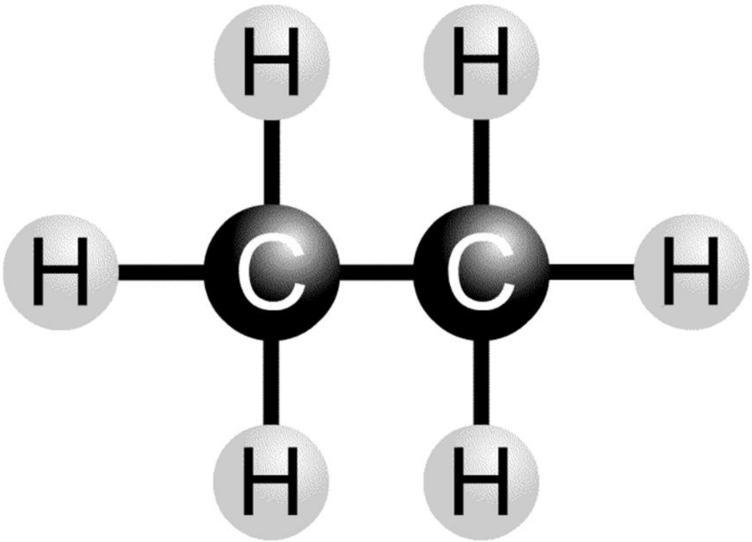
nickel catalyst and high pressure



Organic Chemistry

Reactions of the Alkenes – Addition

nickel catalyst and high pressure

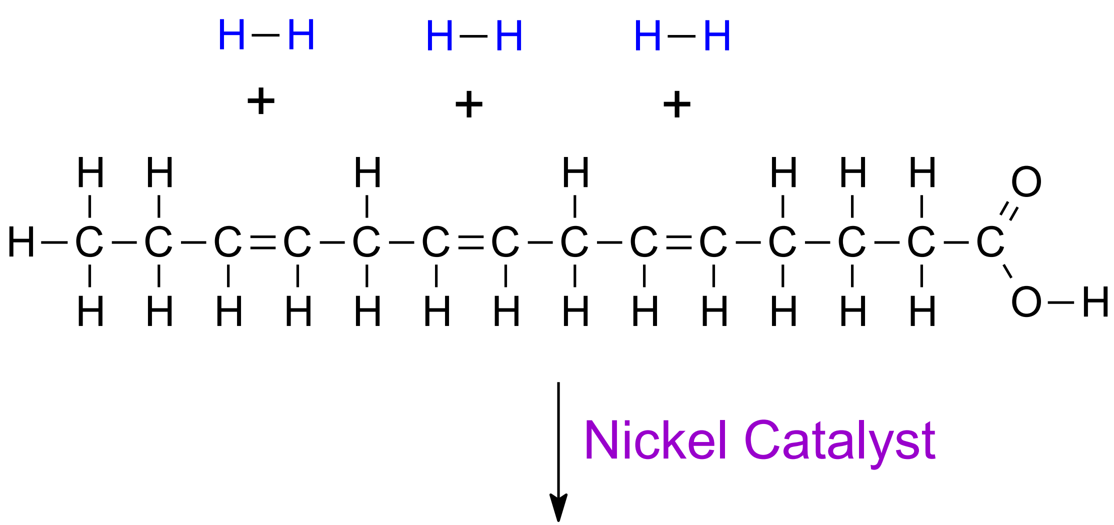


Organic Chemistry

Reactions of the Alkenes – Addition

A molecule that contains more than one carbon-to-carbon double covalent bond is said to be *polyunsaturated*. The catalytic hydrogenation of polyunsaturated plant oils to produce solid fats is used in the manufacture of margarine.

Liquid



Organic Chemistry

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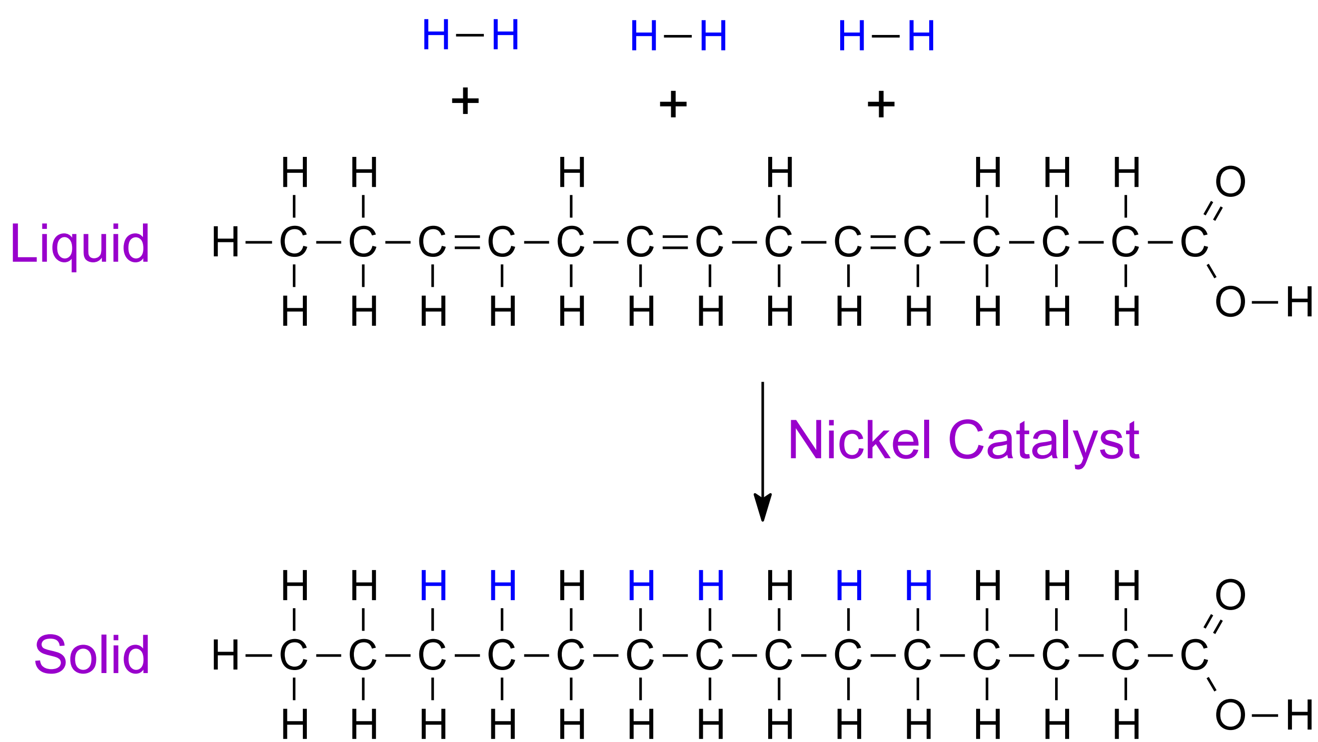
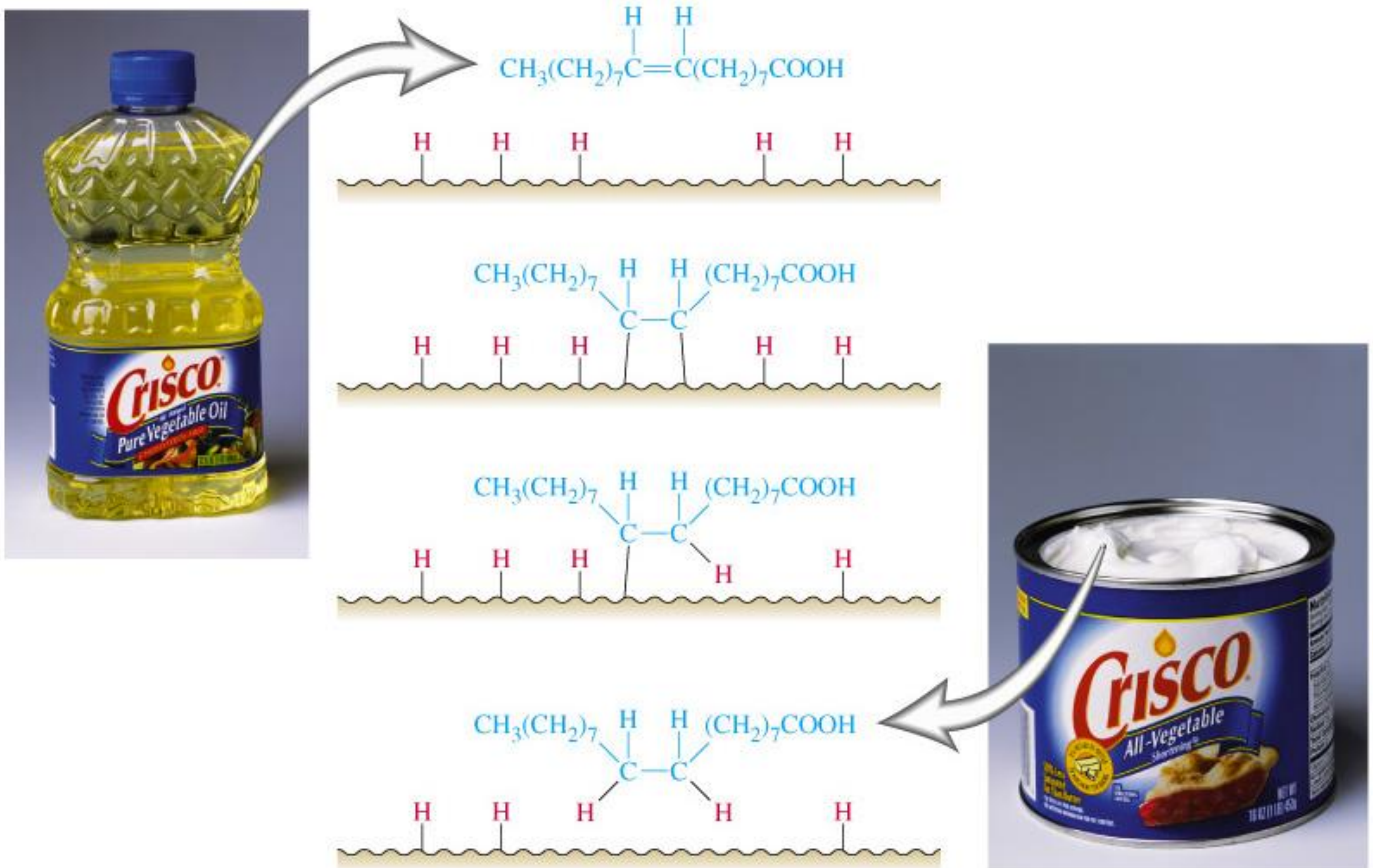


Organic Chemistry

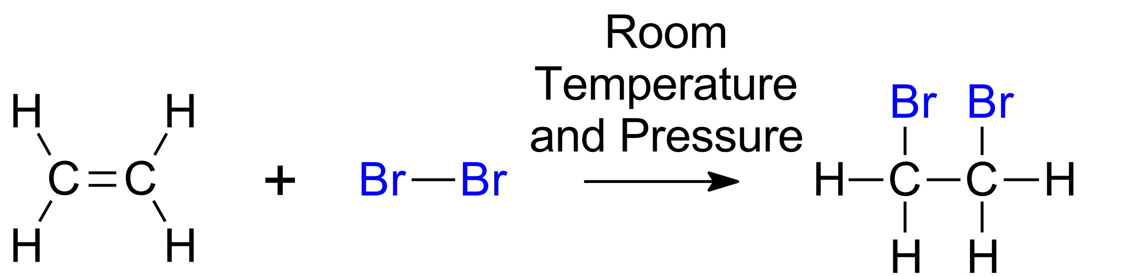
Reactions of the Alkenes – Addition



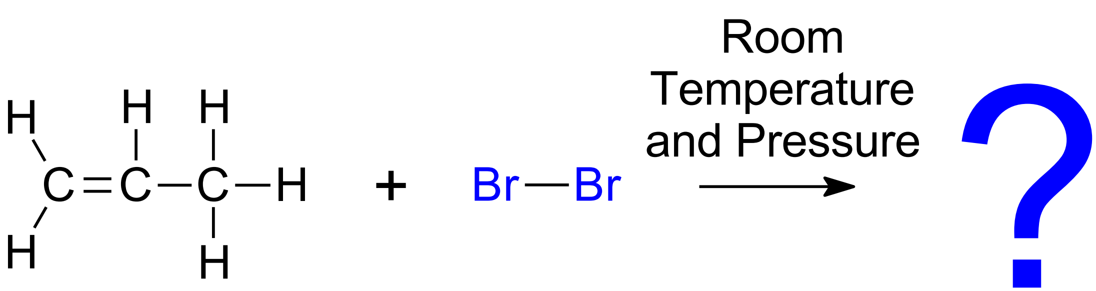
Organic Chemistry

Reactions of the Alkenes – Addition

Alkenes (unsaturated hydrocarbons) react with Group 17 elements at room temperature and pressure to form a halogenoalkane. This is an addition reaction.



Ethene Bromine 1,2-Dibromoethane



Propene Bromine

Organic Chemistry

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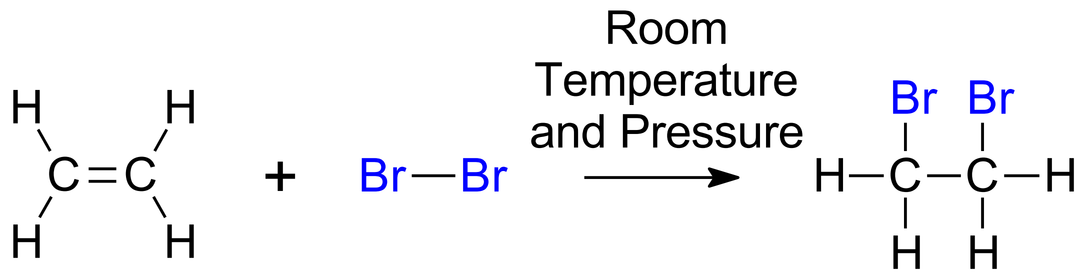
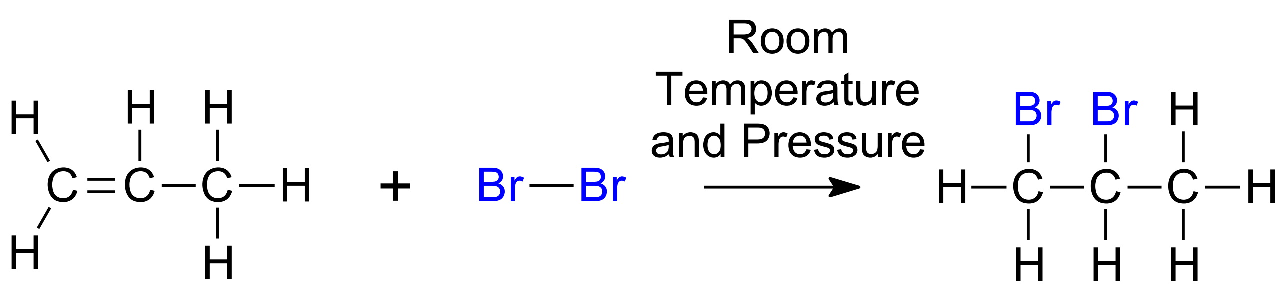


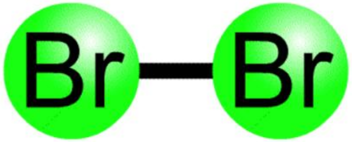
Ethene Bromine 1,2-Dibromoethane



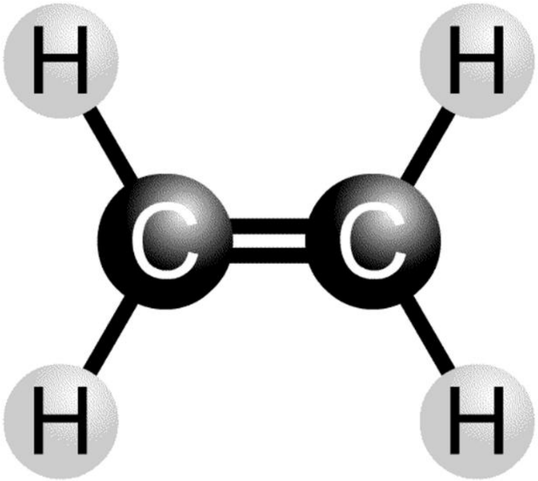
Propene Bromine 1,2-Dibromopropane

Organic Chemistry

Reactions of the Alkenes – Addition



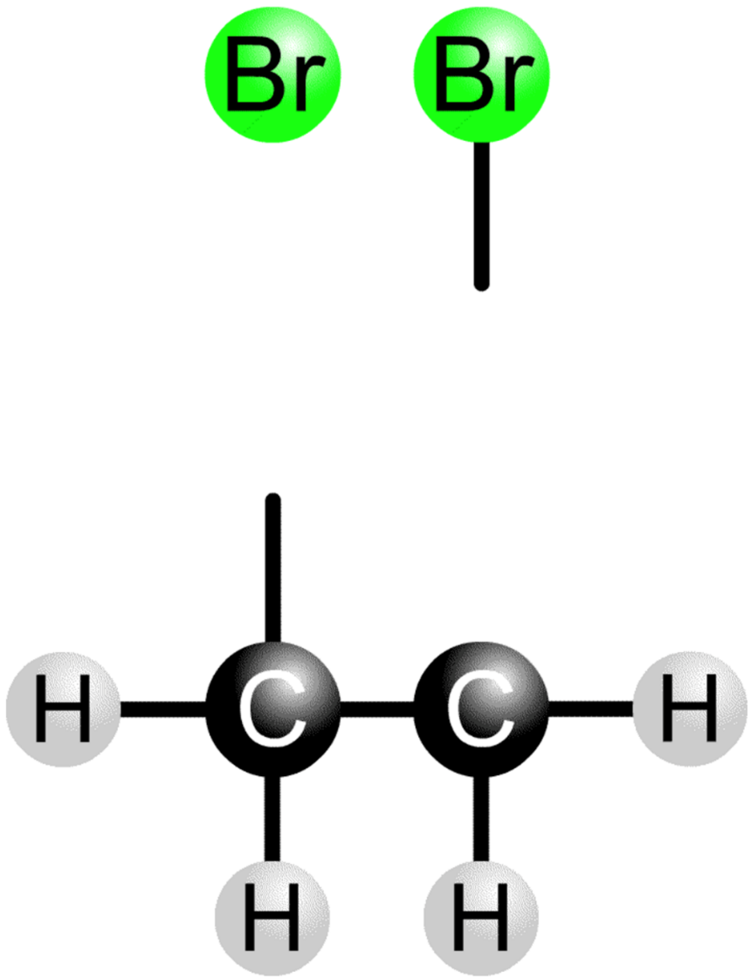
room
temperature
and pressure



Organic Chemistry

Reactions of the Alkenes – Addition

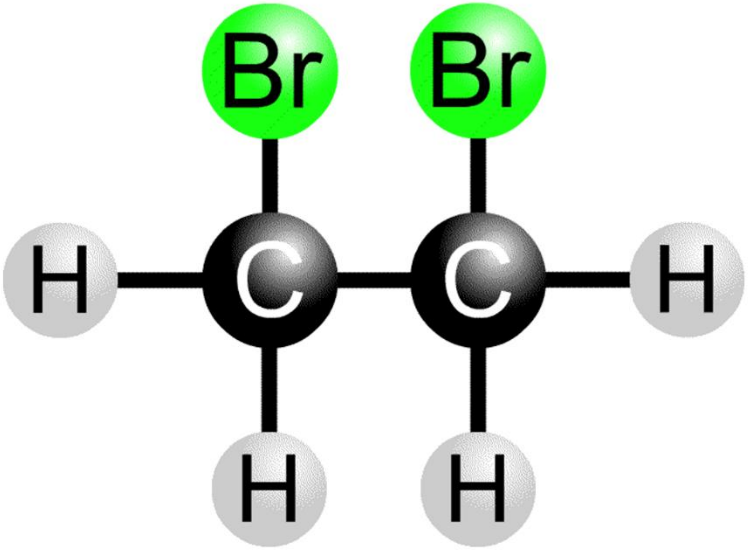
room
temperature
and pressure



Organic Chemistry

Reactions of the Alkenes – Addition

room temperature and pressure

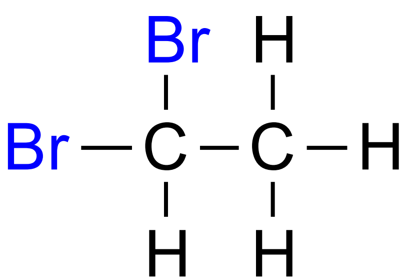


Organic Chemistry

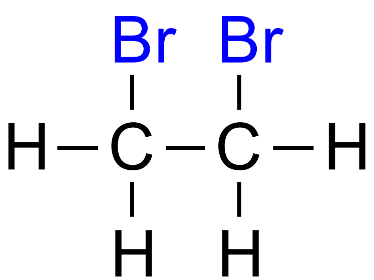
Reactions of the Alkenes – Addition

Formative Assessment:

How would you prepare these two compounds?



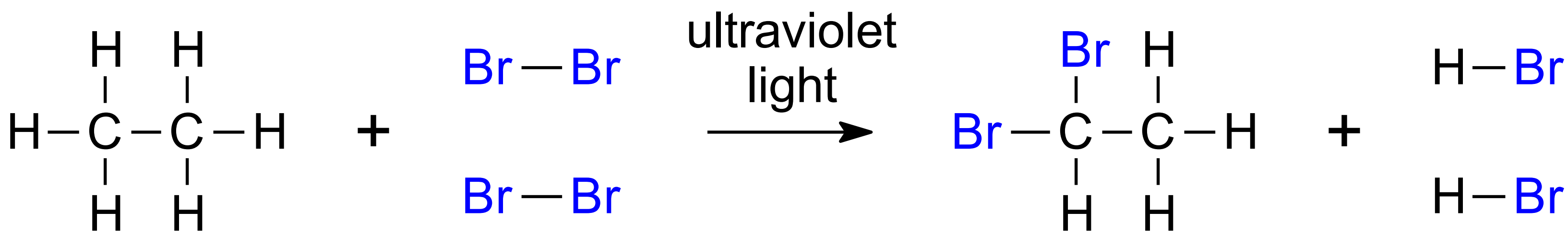
1,1-dibromoethane



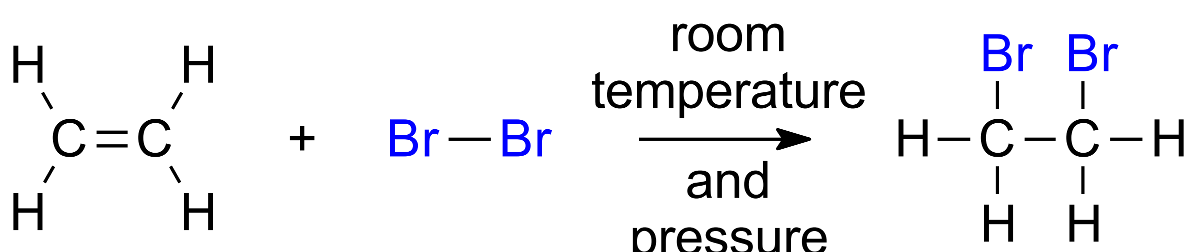
1,2-dibromoethane

Organic Chemistry

Reactions of the Alkenes – Addition



Ethane 1,1-dibromoethane



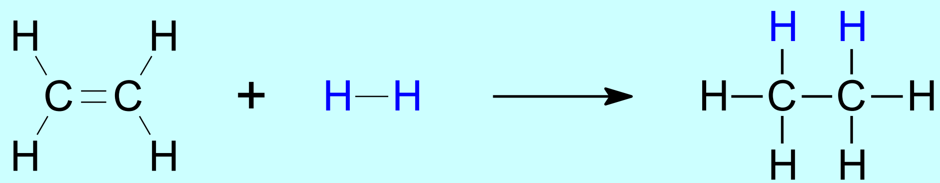
Ethene 1,2-dibromoethane

Organic Chemistry

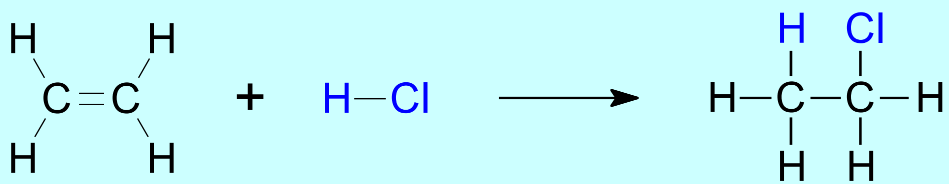
Reactions of the Alkenes – Addition

IMPORTANT NOTE

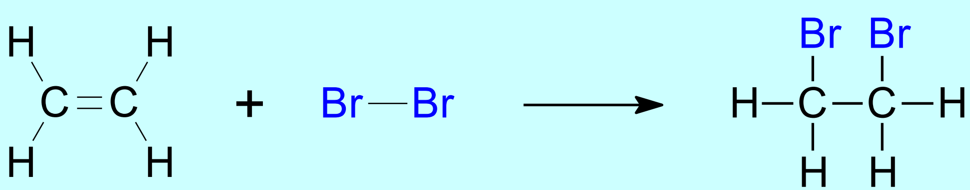
- The product of an addition reaction is no longer an alkene, so its name DOES NOT end –ene.



Ethene | Hydrogen | Ethane



Ethene | Hydrogen Chloride | 1-Chloroethane



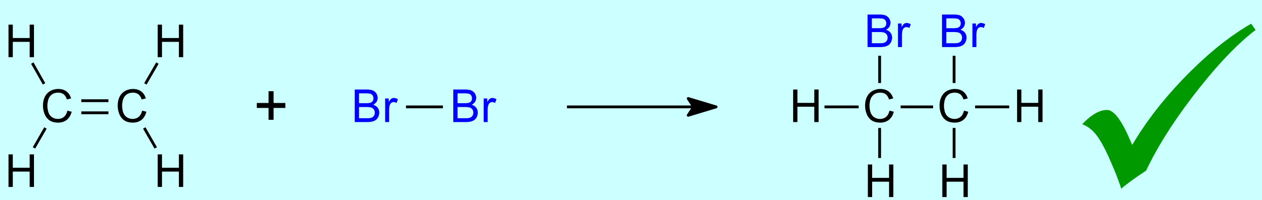
Ethene | Bromine | 1,2-Dibromoethane

Organic Chemistry

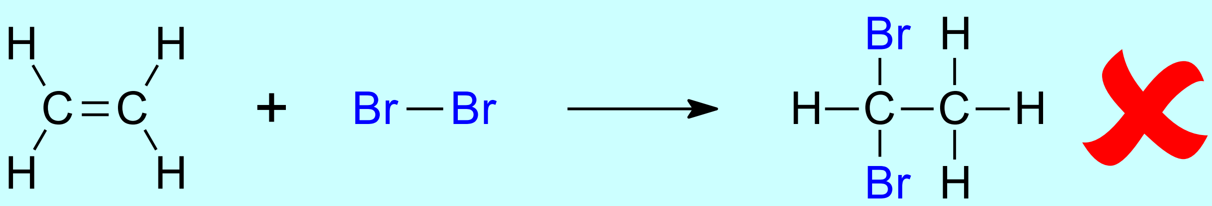
Reactions of the Alkenes – Addition

IMPORTANT NOTE

- Bromine adds *across* the C=C bond. Each of the two bromine atoms bonds to a *different* carbon atom.

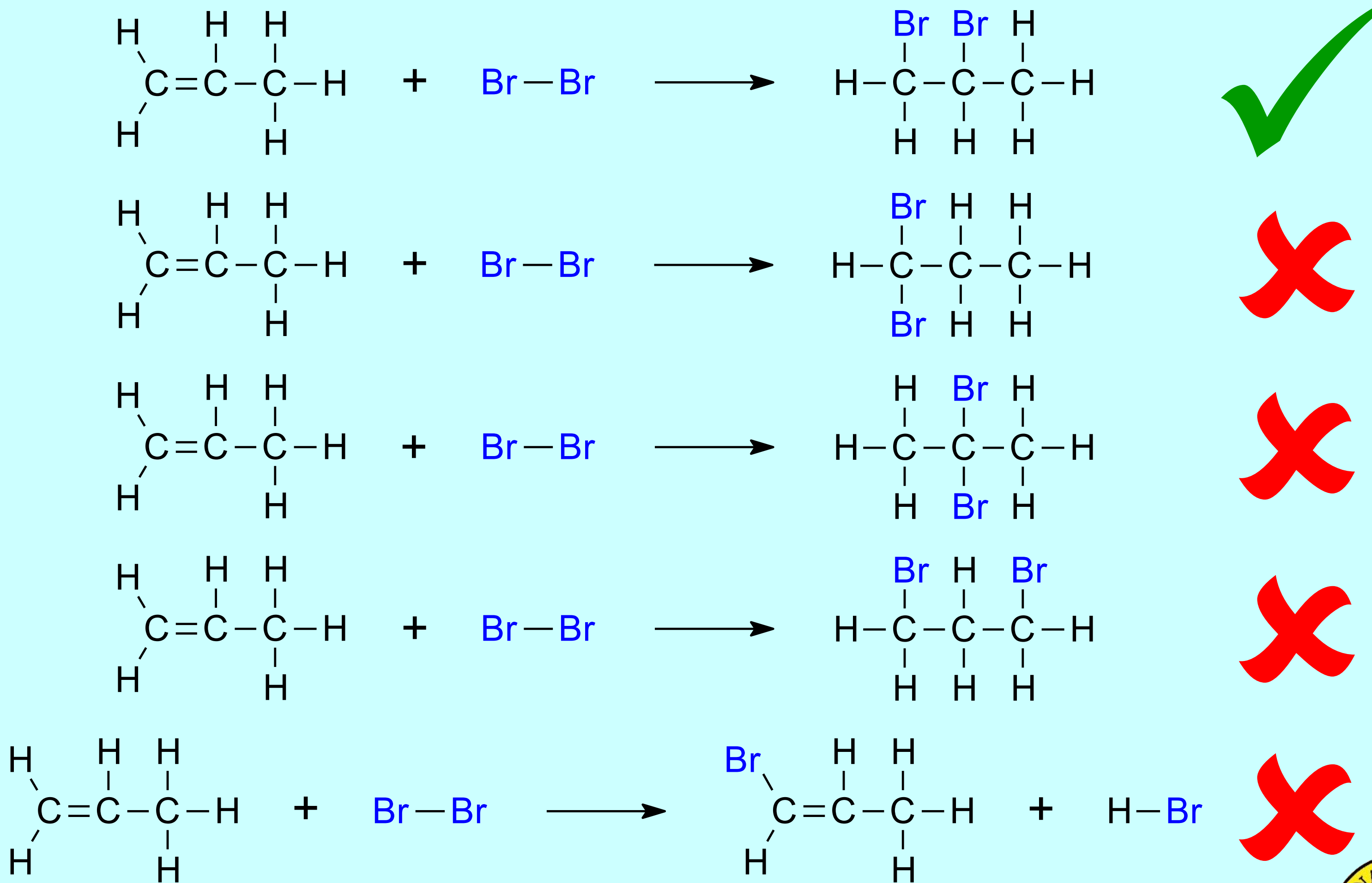


- The two bromine atoms DO NOT bond to the *same* carbon atom.



Organic Chemistry

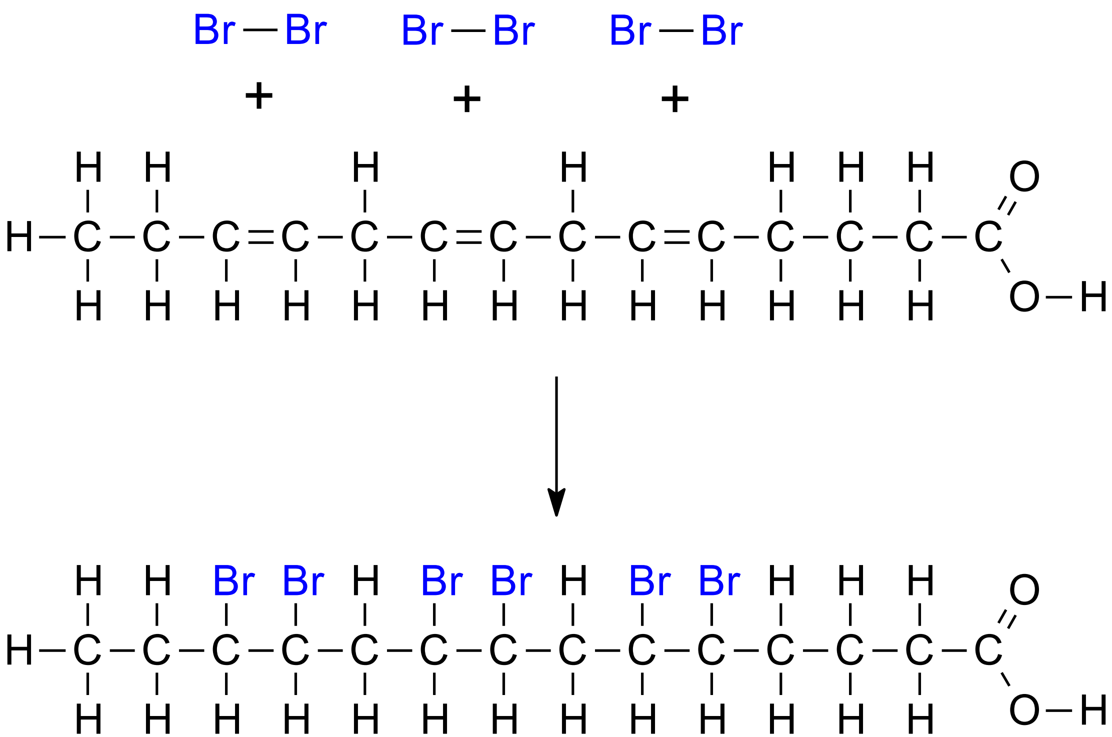
Reactions of the Alkenes – Addition



Organic Chemistry

Reactions of the Alkenes – Addition

The number of carbon-to-carbon double covalent bonds that are present in a molecule can be determined by reacting it with bromine. In this example, 1 mol of the organic compound reacts with 3 mol of bromine, so one molecule must contain three carbon-to-carbon double covalent bonds.



Organic Chemistry

Reactions of the Alkenes – Addition

The colour change of bromine water from reddish-brown to colourless is an important qualitative test for an alkene.

Organic Chemistry

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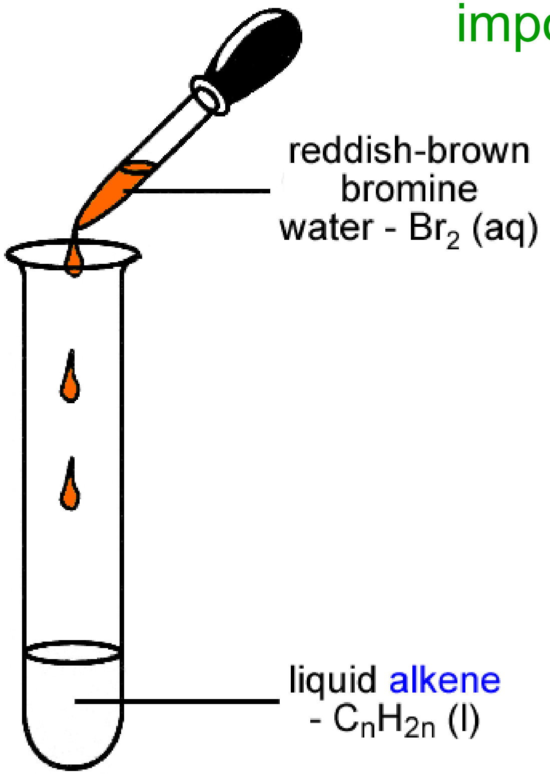

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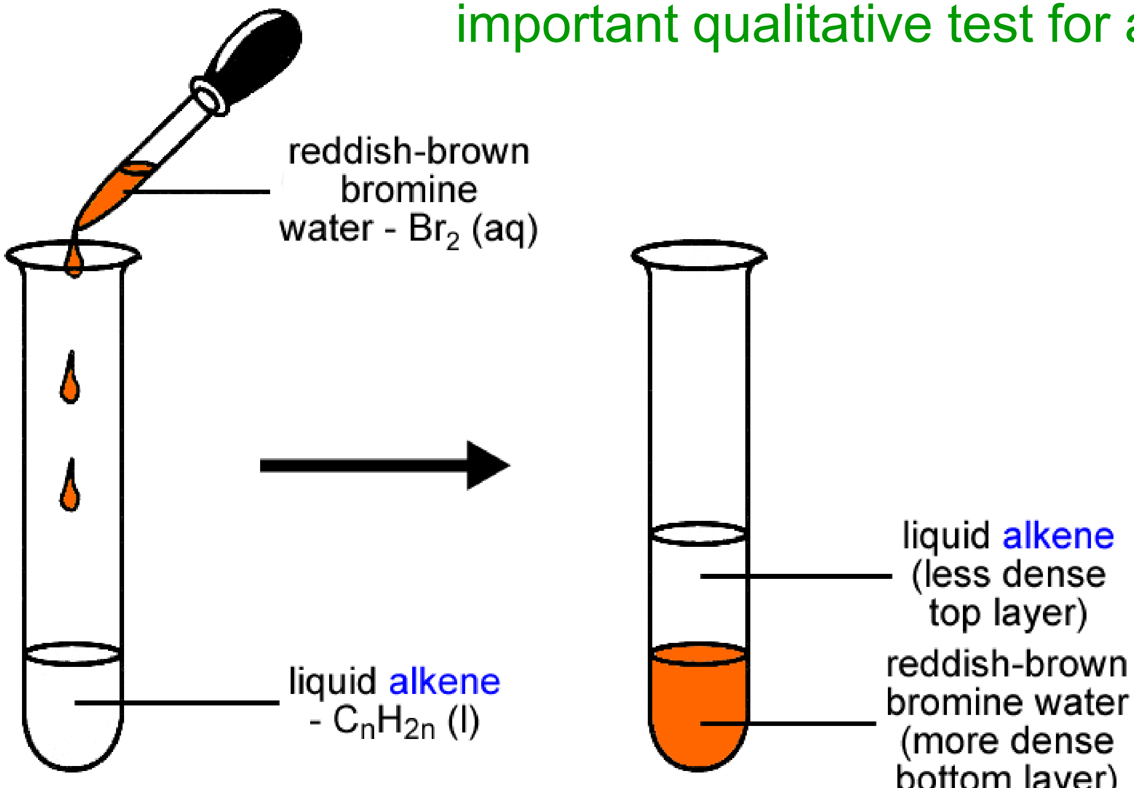

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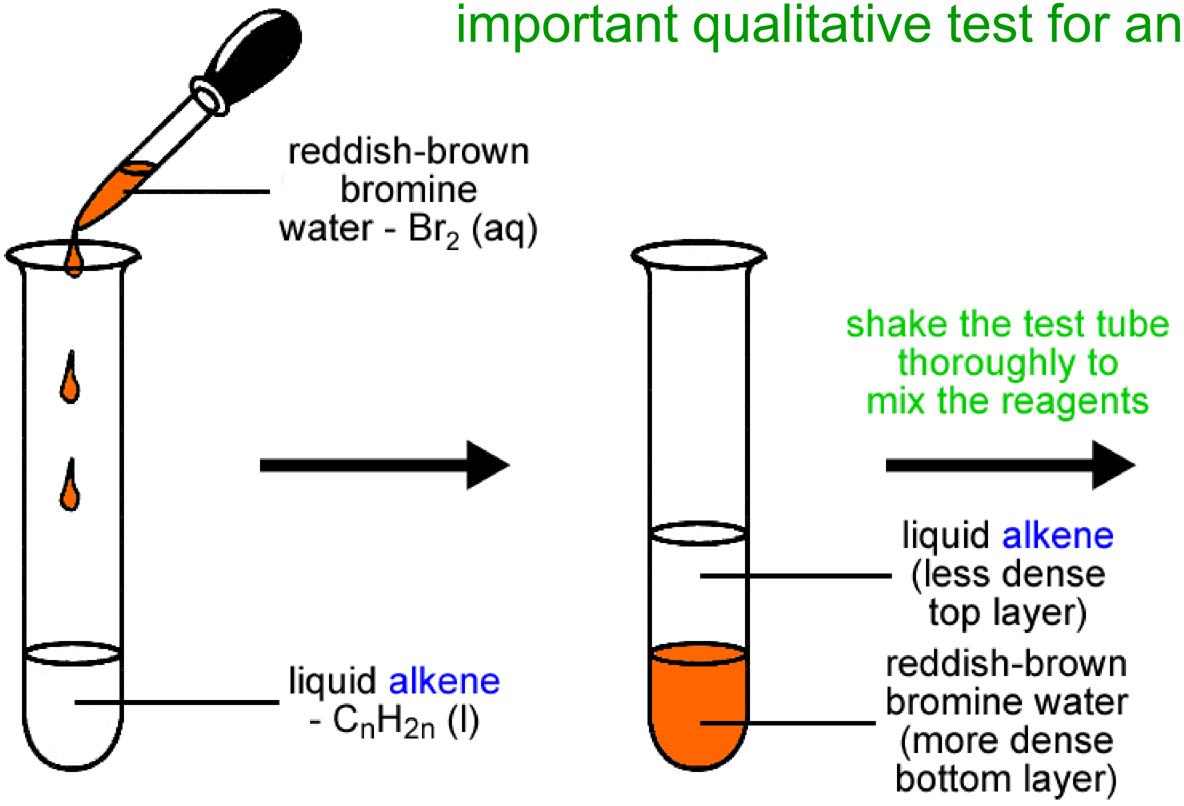

Organic Chemistry

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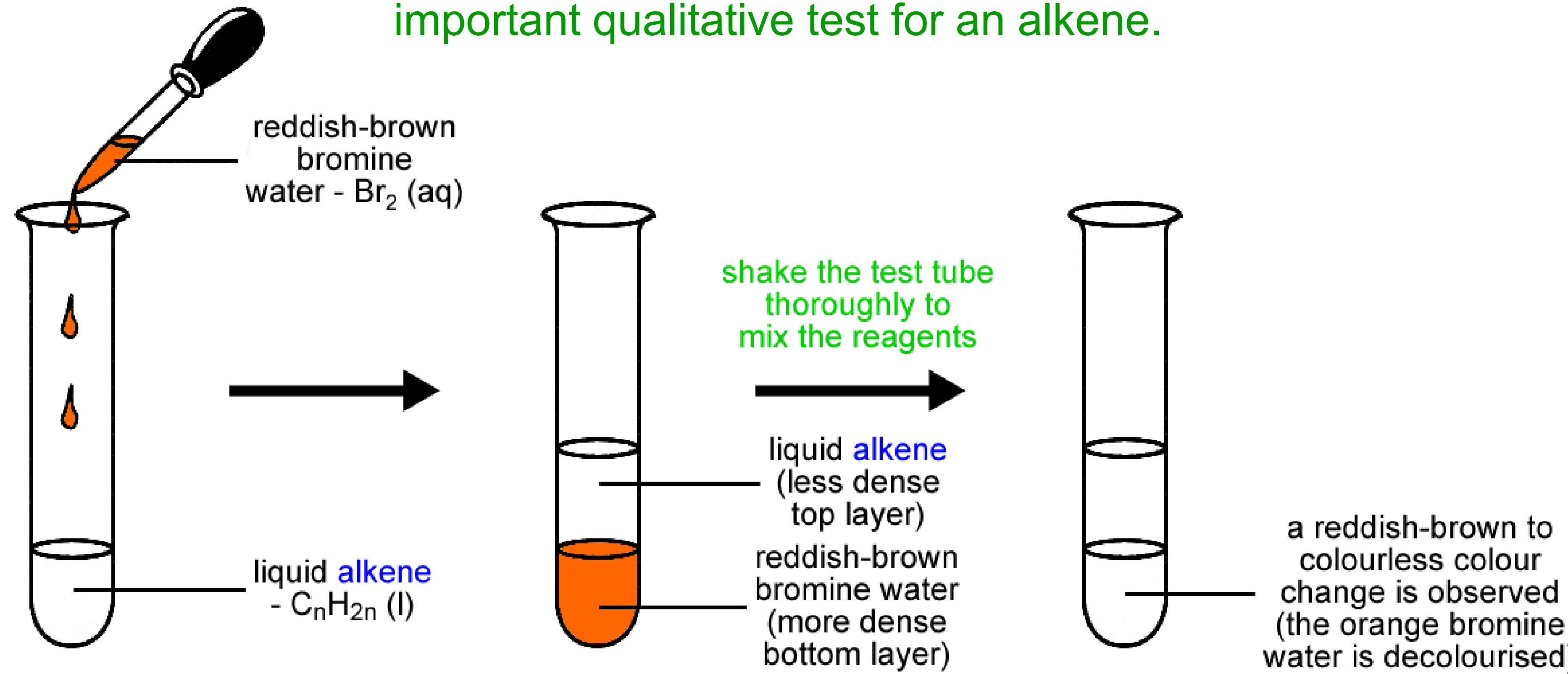
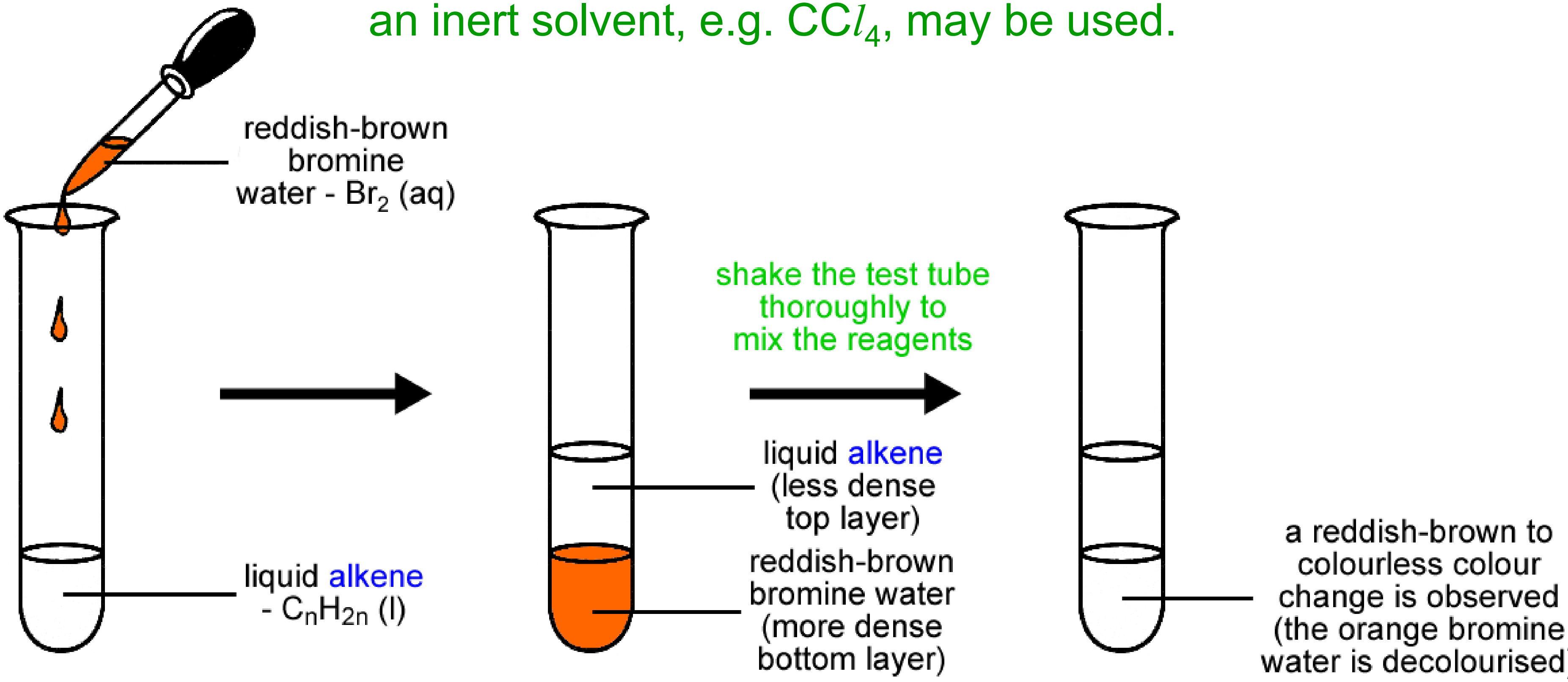


Organic Chemistry

Reactions of the Alkenes – Addition

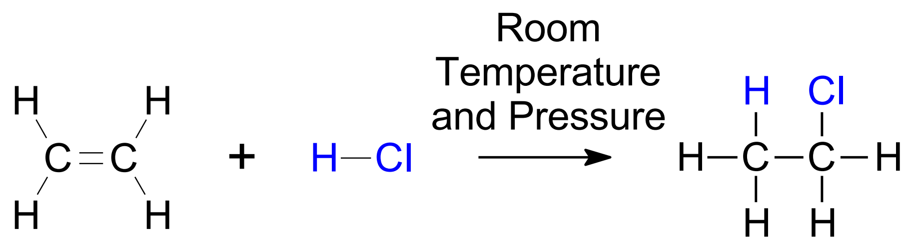
Note: In addition to using bromine water, a solution of bromine dissolved in an inert solvent, e.g. CCl_4, may be used.



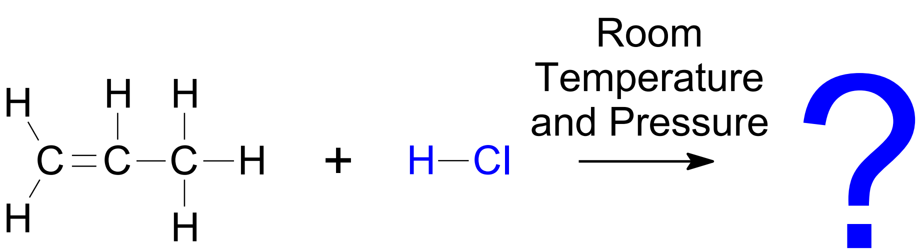
Organic Chemistry

Reactions of the Alkenes – Addition

Alkenes (unsaturated hydrocarbons) react with hydrogen halides at room temperature and pressure to form a halogenoalkane. This is an addition reaction.



Ethene
Hydrogen Chloride
1-Chloroethane

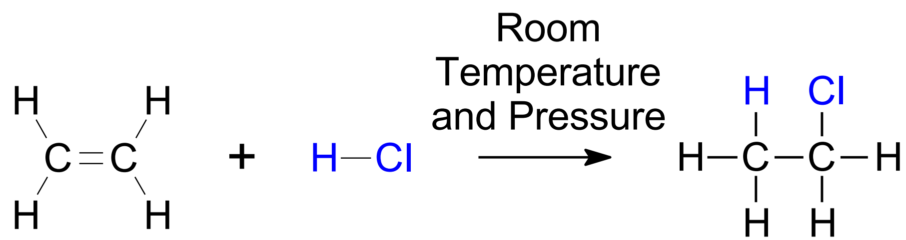


Propene
Hydrogen Chloride

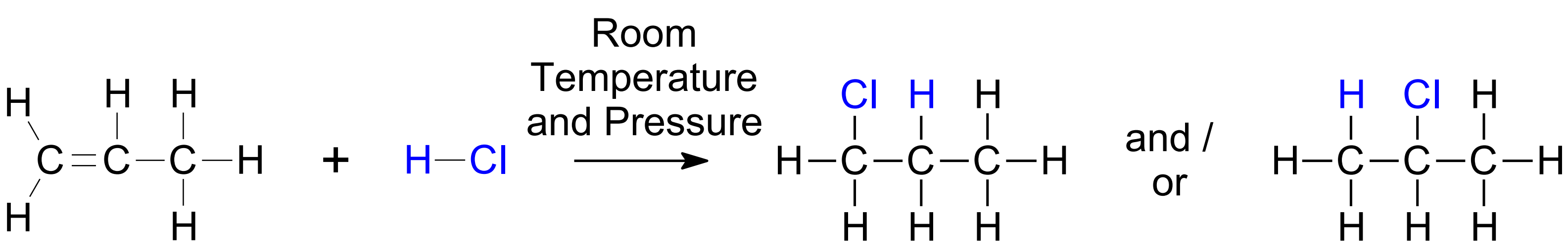
Organic Chemistry

Reactions of the Alkenes – Addition

Alkenes (unsaturated hydrocarbons) react with hydrogen halides at room temperature and pressure to form a halogenoalkane. This is an addition reaction.



Ethene | Hydrogen Chloride | 1-Chloroethane



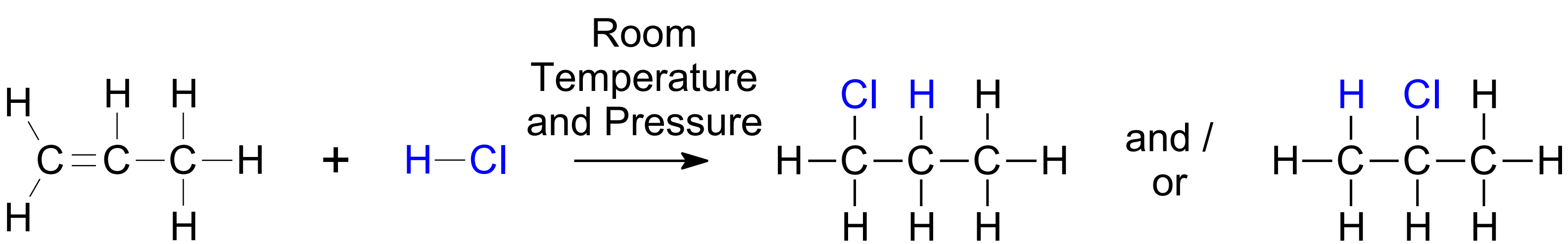
Propene | Hydrogen Chloride | 1-Chloropropane | 2-Chloropropane

Organic Chemistry

Reactions of the Alkenes – Addition – Enrichment

Note: Where an alkene could react to form more than one reaction product, the most favourable reaction product can be predicted by *Markovnikov's rule*.

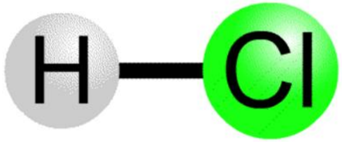
Markovnikov's rule states that, in a reaction where a hydrogen halide (H–X, where X is C*l*, Br or I) adds across the C=C bond of an alkene, the hydrogen atom of H–X will bond to the carbon of the alkene that already has the most hydrogen atoms bonded to it. Hence, in the example given below, *2-chloropropane* will be the favoured product.



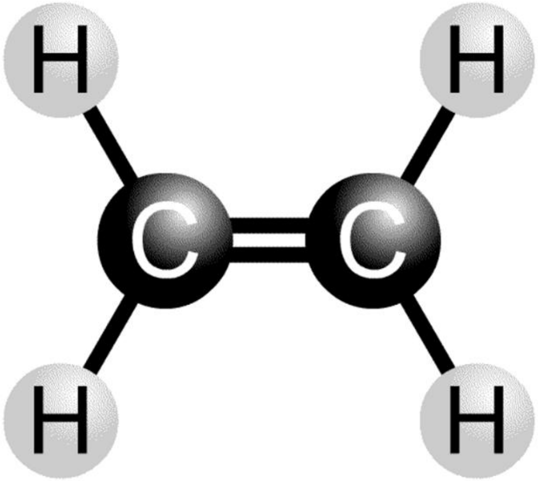
Propene + Hydrogen Chloride → 1-Chloropropane and / or 2-Chloropropane

Organic Chemistry

Reactions of the Alkenes – Addition



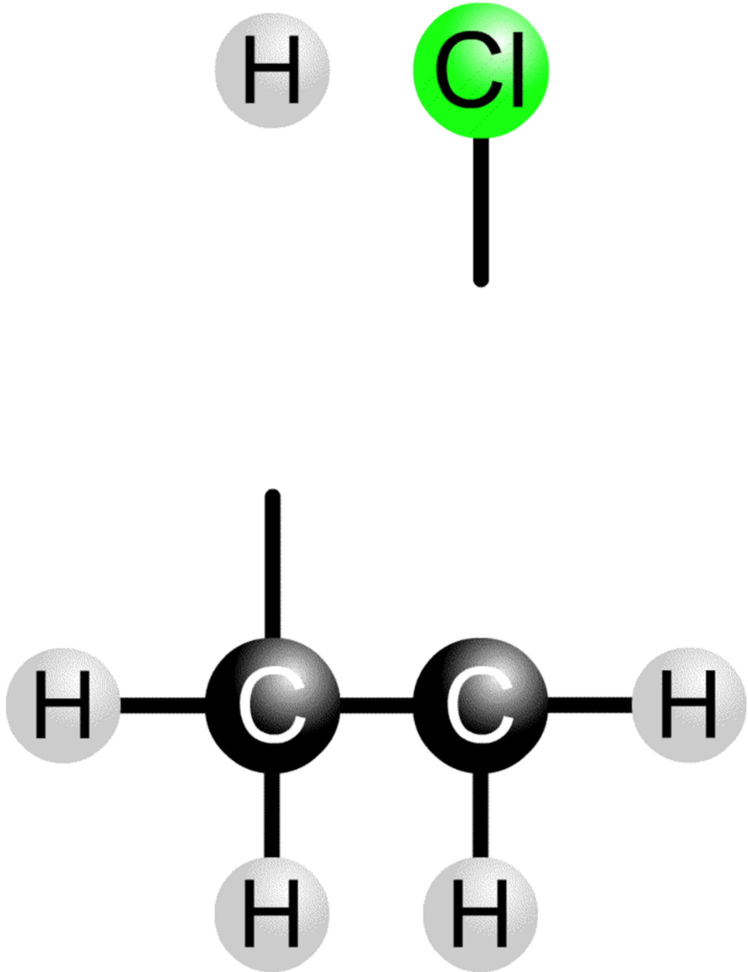
room
temperature
and pressure



Organic Chemistry

Reactions of the Alkenes – Addition

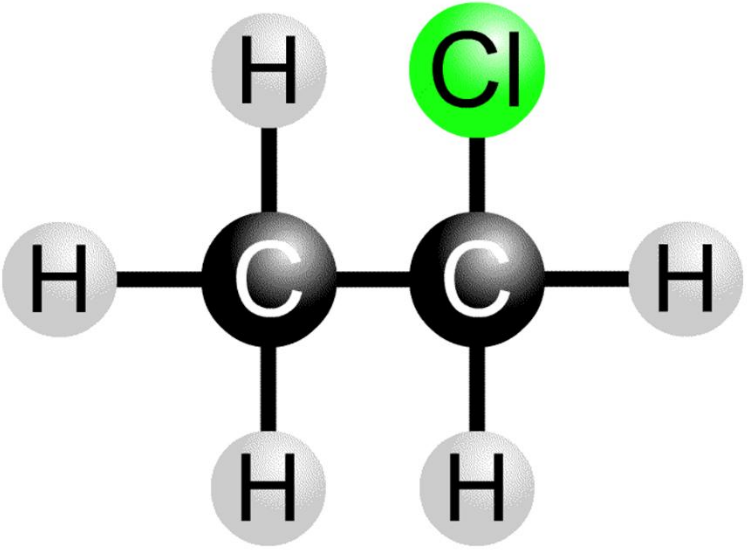
room temperature and pressure



Organic Chemistry

Reactions of the Alkenes – Addition

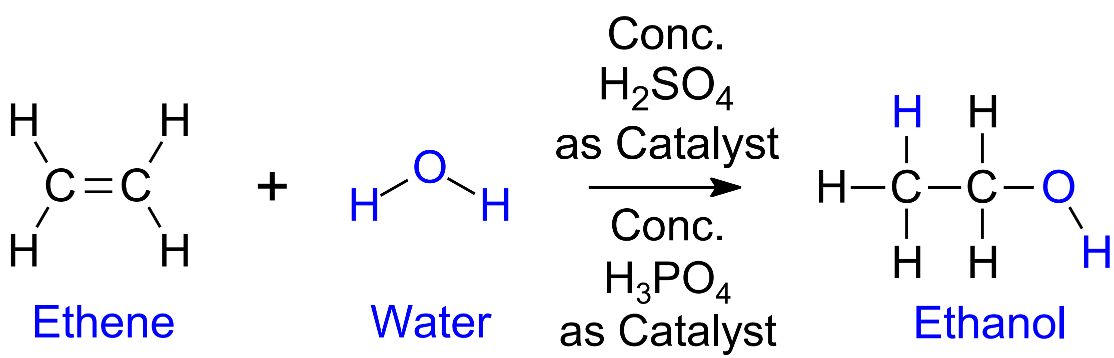
room temperature and pressure

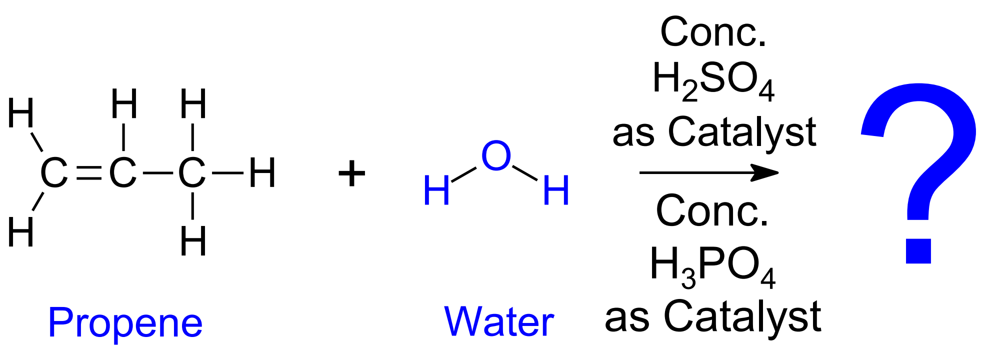


Organic Chemistry

Reactions of the Alkenes – Addition

Alkenes (unsaturated hydrocarbons) react with water in the presence of an acid catalyst to form an alcohol. This is an example of an addition reaction.





Organic Chemistry

Reactions of the Alkenes – Addition

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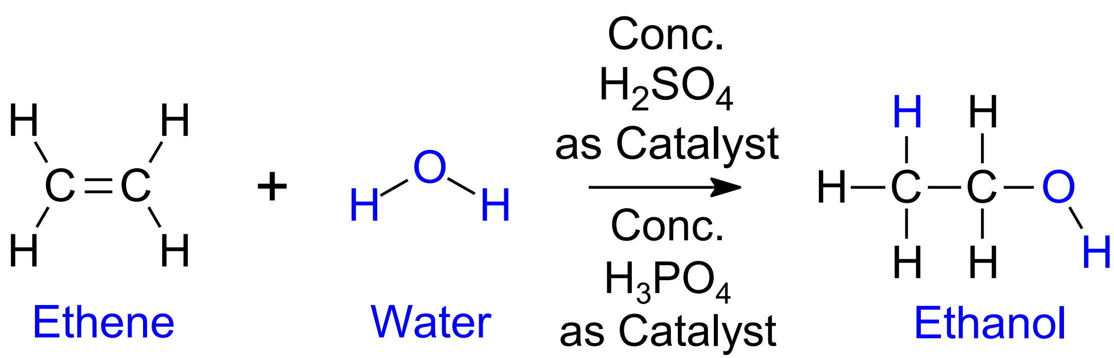
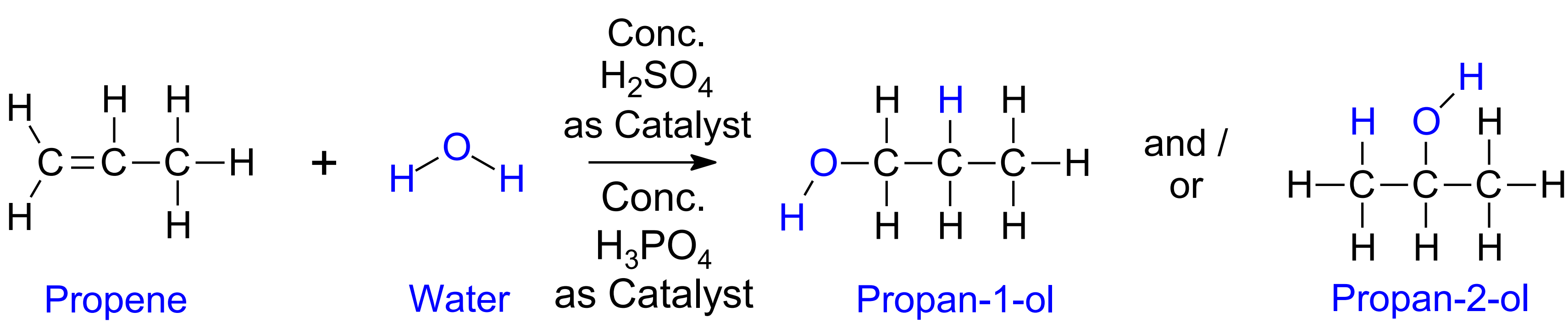
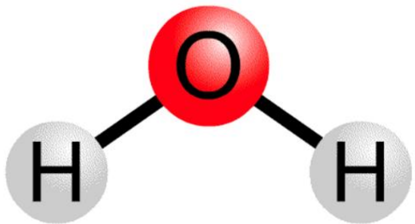


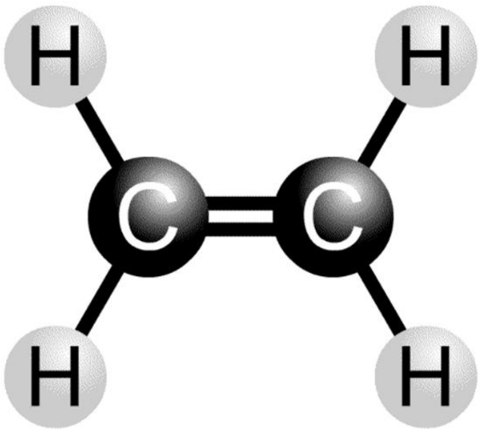


Organic Chemistry

Reactions of the Alkenes – Addition



conc.
H_3PO_4
catalyst



Organic Chemistry

Reactions of the Alkenes – Addition

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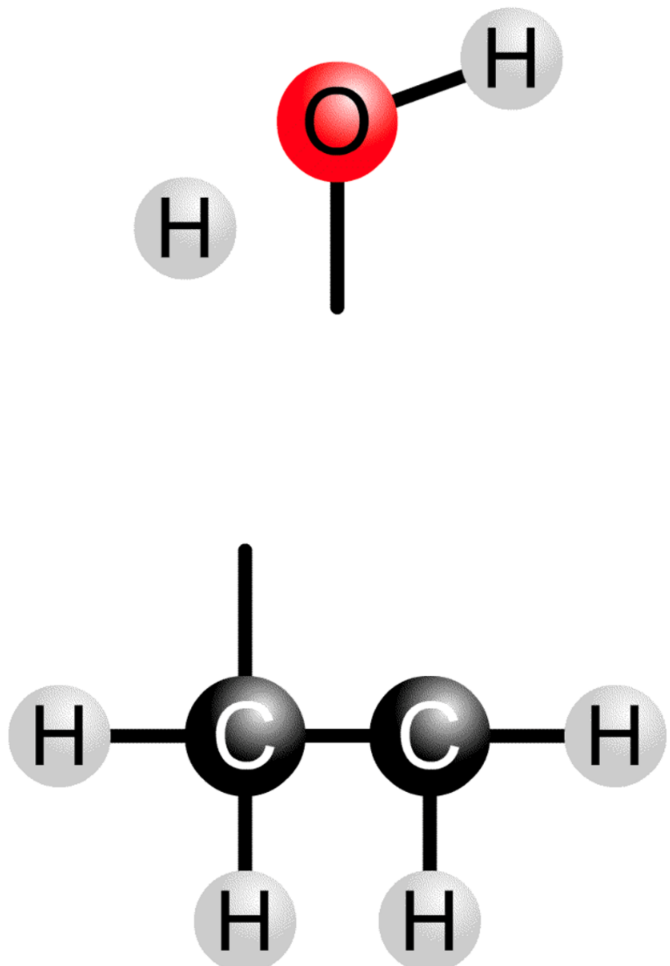
H_3PO_4
catalyst



Organic Chemistry

Reactions of the Alkenes – Addition

conc.
H_3PO_4
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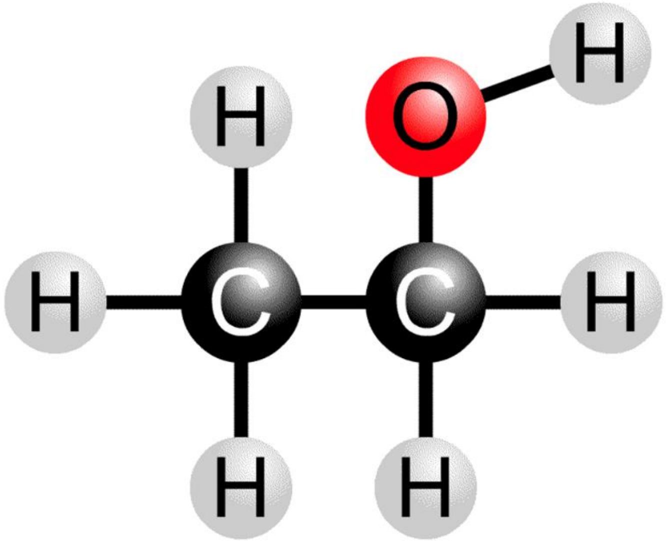
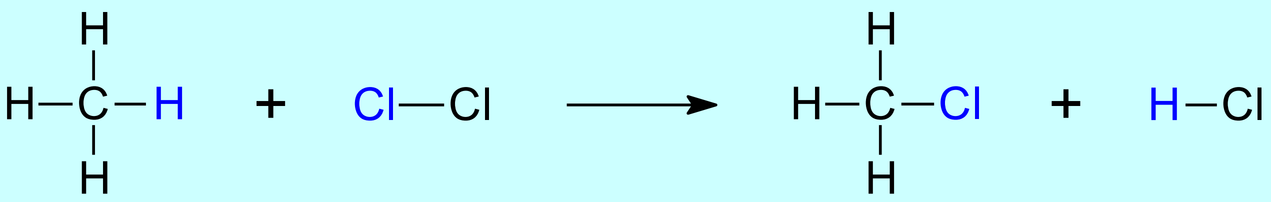


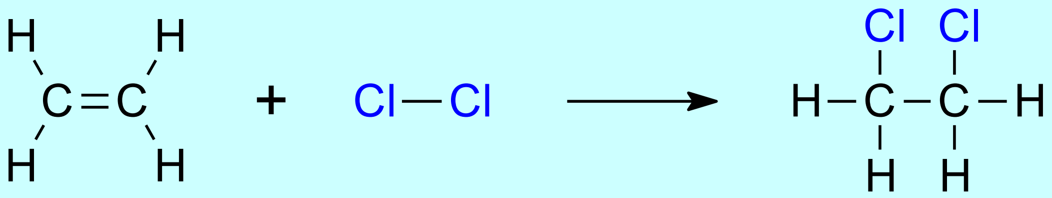
Organic Chemistry

Compare the Reactions of Alkanes and Alkenes with Halogens

- Alk<u>ane</u> and a halogen: *Substitution* reaction in the presence of ultraviolet light.



- Alk<u>ene</u> and a halogen: *Addition* reaction at room temperature and pressure (no U.V. light required).

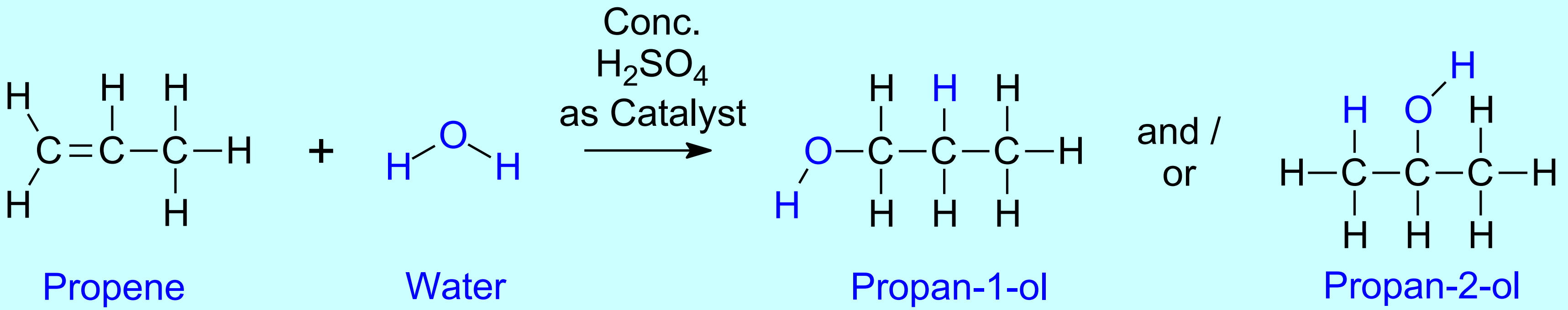


Organic Chemistry

- Which one of the following is the best way of preparing a sample of propan-2-ol?

a) Reacting *propene* with water in the presence of an acid catalyst (addition reaction).

b) Reacting *2-bromopropane* with aqueous sodium hydroxide (substitution reaction).



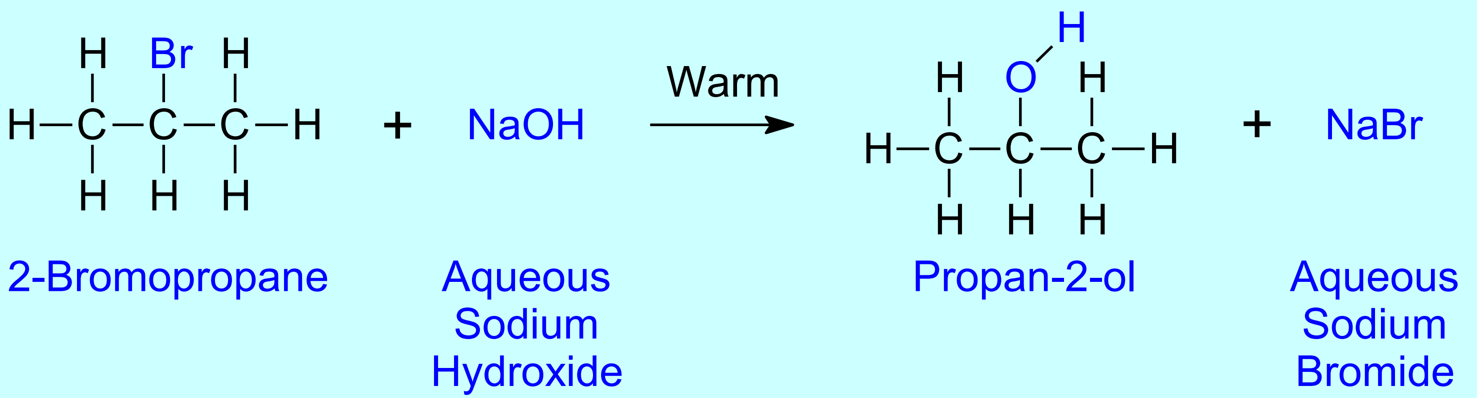
- Using *propene* will produce a *mixture* of *two* organic reaction products (low yield of each isomer).

Organic Chemistry

- Which one of the following is the best way of preparing a sample of propan-2-ol?

a) Reacting *propene* with water in the presence of an acid catalyst (addition reaction).

b) Reacting *2-bromopropane* with aqueous sodium hydroxide (substitution reaction).



- Using *2-bromopropane* is preferred because it will produce only *one* organic reaction product (high yield).

Organic Chemistry

What are the essential reactions of the *alcohols*?

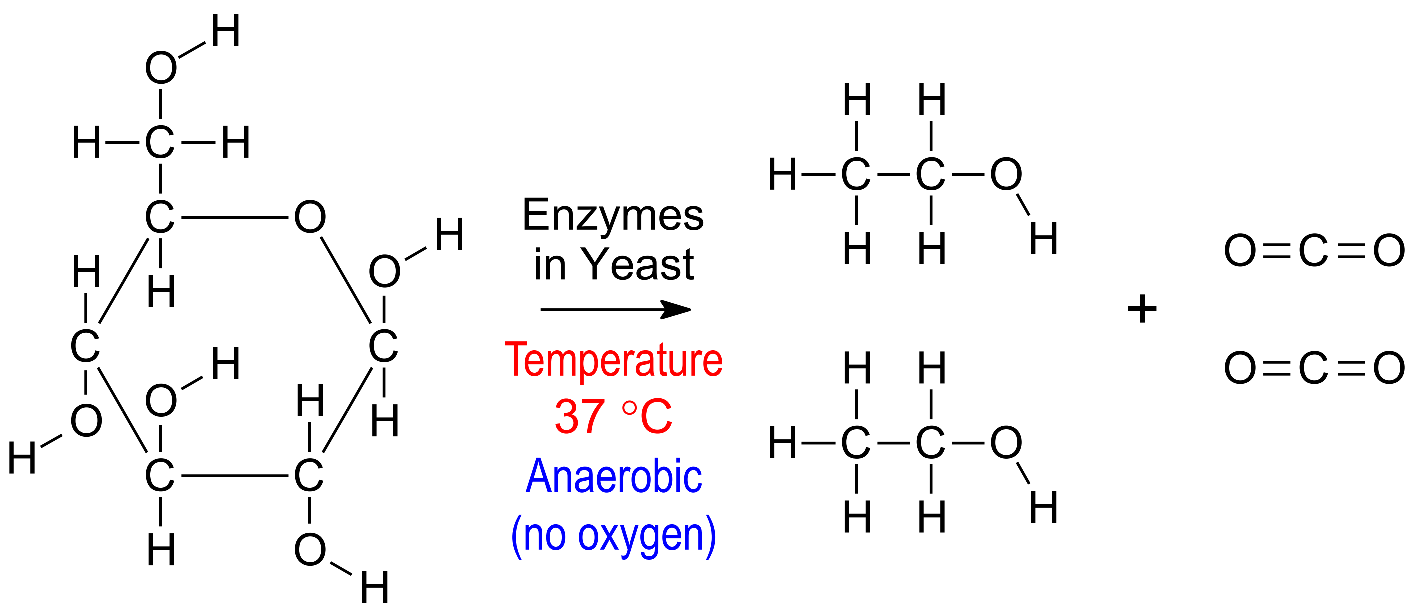
- Preparation
- Combustion
- Substitution
- Dehydration
- Oxidation
- Sodium

Organic Chemistry

Reactions of the Alcohols – Preparation

Ethanol can be produced by the fermentation of glucose.

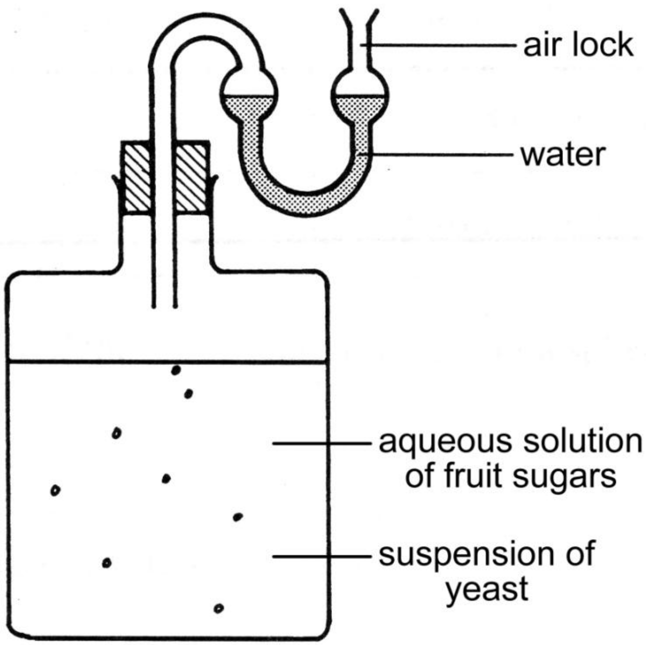
$$C_6H_{12}O_6(aq) \rightarrow 2CH_3CH_2OH(aq) + 2CO_2(g)$$



Glucose Ethanol Carbon Dioxide

Organic Chemistry

Reactions of the Alcohols – Preparation



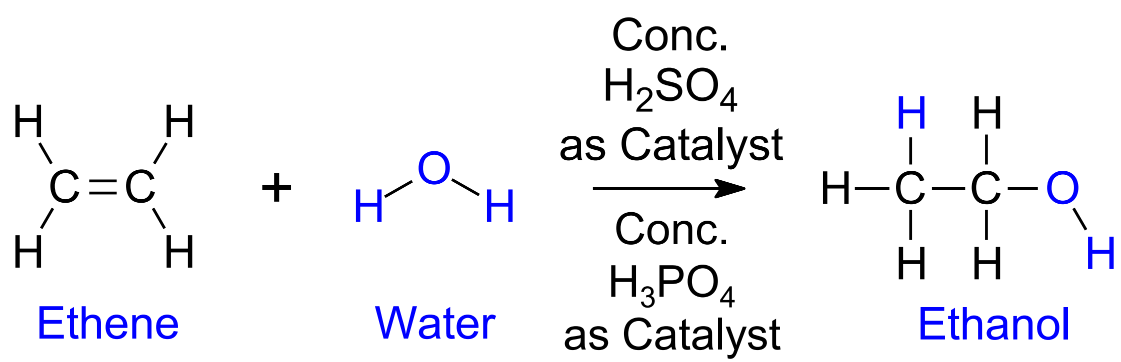
- *Enzymes* in the yeast increase the rate of the reaction by *lowering* the *activation energy*.
- The optimum temperature is 37°C. At higher temperatures, the enzymes in the yeast are *denatured*.
- The air lock allows CO_2 (g) to escape while preventing O_2 (g) from entering the container. O_2 (g) will *oxidise* the ethanol to ethanoic acid (vinegar).
- Ethanol is obtained by *distillation* of the reaction mixture.

Organic Chemistry

Reactions of the Alcohols – Preparation

Remember, ethanol can be prepared by reacting ethene with water in the presence of concentrated sulfuric acid as a catalyst. This is an addition reaction.

$$C_2H_4(g) + H_2O(l) \rightarrow CH_3CH_2OH(l)$$

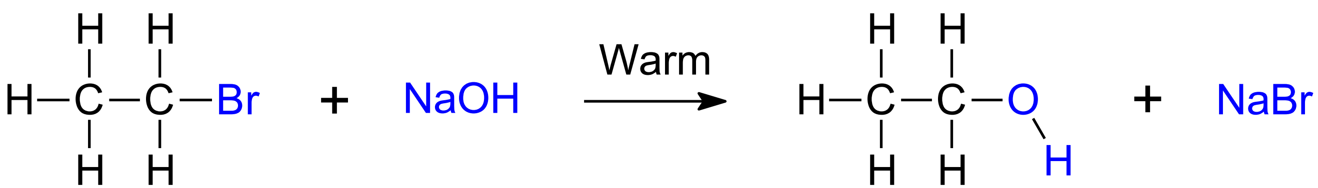


Organic Chemistry

Reactions of the Alcohols – Preparation

Remember, ethanol can be prepared by warming bromoethane with aqueous sodium hydroxide. This is a substitution reaction.

$$CH_3CH_2Br(l) \ + \ NaOH(aq) \rightarrow CH_3CH_2OH(l) \ + \ NaBr(aq)$$



Bromoethane | Aqueous Sodium Hydroxide | Ethanol | Aqueous Sodium Bromide

Organic Chemistry

Reactions of the Alcohols – Combustion

- Alcohols undergo complete combustion to form carbon dioxide and water as the reaction products.

- This *exothermic* reaction releases energy that can be used to power certain automobiles.

ethanol + oxygen → carbon dioxide + water

$$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(g)$$

propanol + oxygen → carbon dioxide + water

$$2C_3H_7OH(l) + 9O_2(g) \rightarrow 6CO_2(g) + 8H_2O(g)$$

Organic Chemistry

Reactions of the Alcohols – Substitution

- The hydroxyl group, –OH, of an alcohol can be substituted by a halogen, *e.g.* –C*l* or –Br.
- The reaction converts an alcohol into a halogenoalkane.
- A sodium halide is treated with concentrated sulfuric acid to produce a hydrogen halide, *e.g.*

$$NaBr + H_2SO_4 \rightarrow HBr + NaHSO_4$$

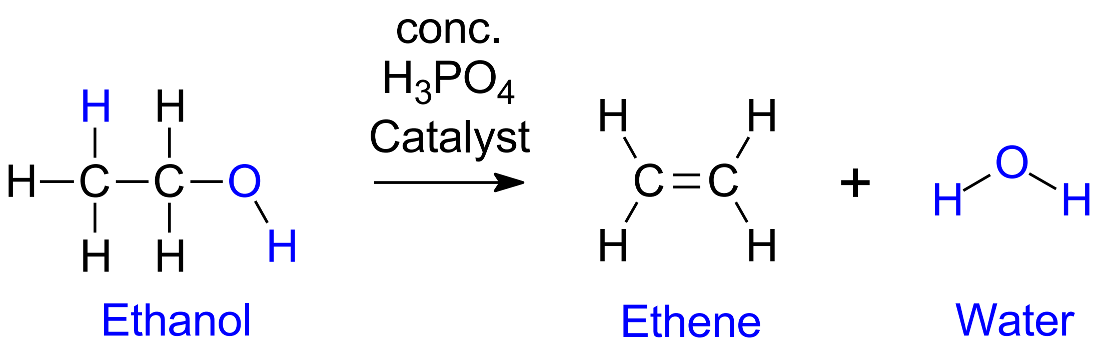
- This mixture is then warmed with the alcohol:

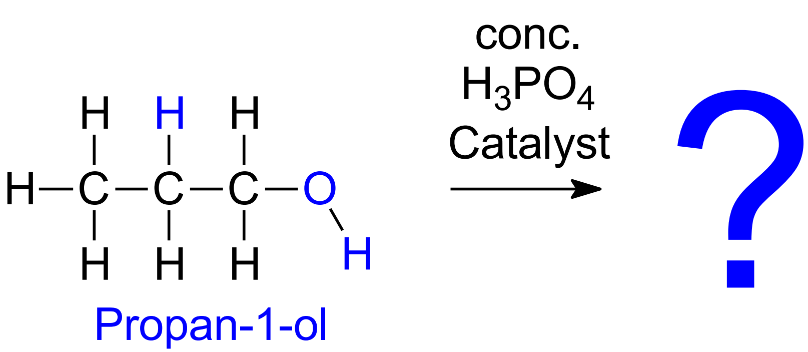
$$CH_3CH_2OH + HBr \rightarrow CH_3CH_2Br + H_2O$$

Organic Chemistry

Reactions of the Alcohols – Dehydration

The dehydration of an alcohol results in the formation of an alkene as the main reaction product. This is an example of an elimination reaction.



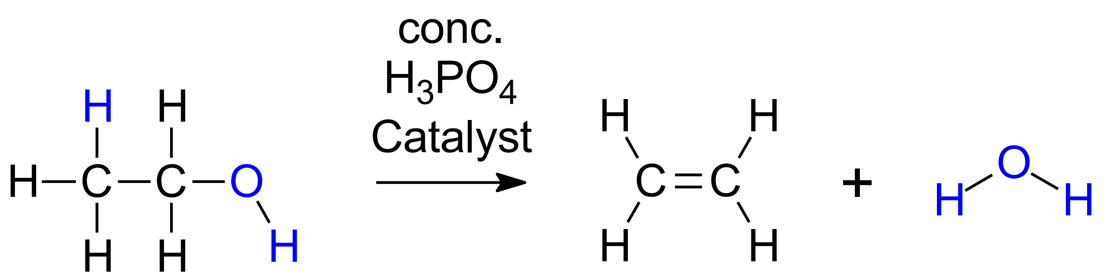


Sulfuric acid can also be used as a catalyst, and the reaction mixture is warmed to approximately 170 °C.

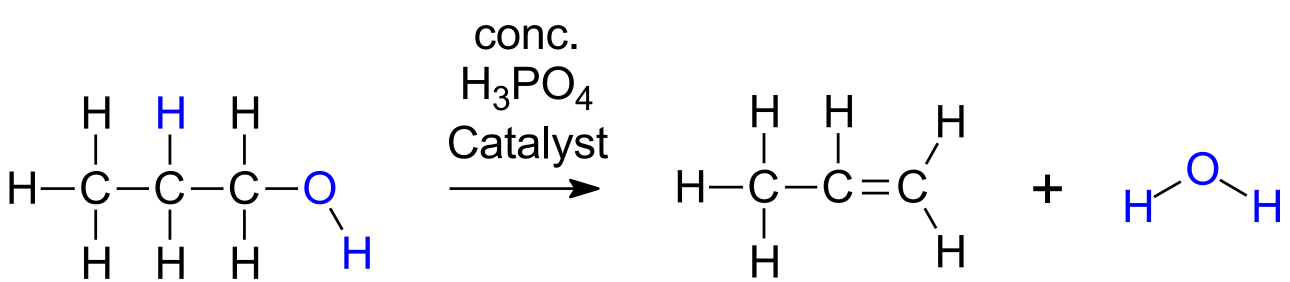
Organic Chemistry

Reactions of the Alcohols – Dehydration

The dehydration of an alcohol results in the formation of an alkene as the main reaction product. This is an example of an elimination reaction.



Ethanol Ethene Water



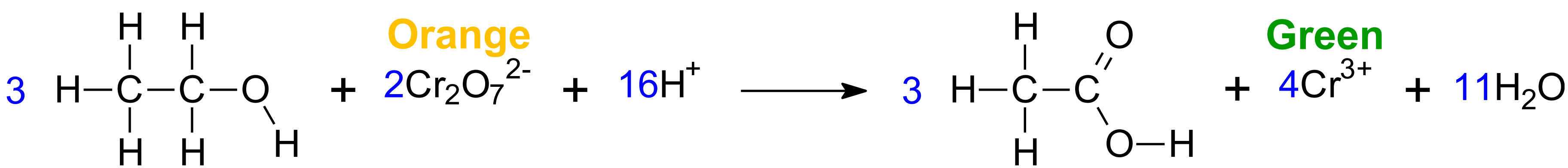
Propan-1-ol Propene Water

Sulfuric acid can also be used as a catalyst, and the reaction mixture is warmed to approximately 170 °C.

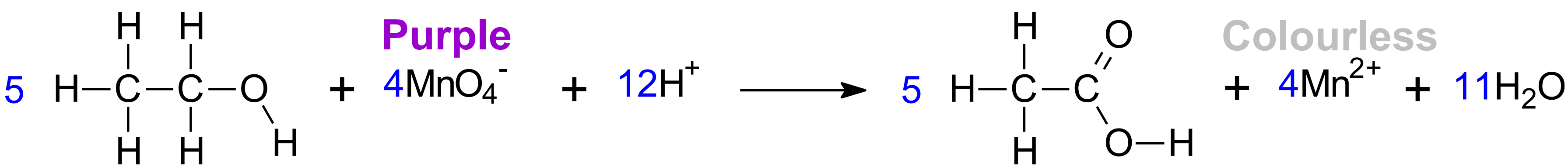
Organic Chemistry

Reactions of the Alcohols – Oxidation

Alcohols can be oxidised to carboxylic acids using **i)** acidified potassium dichromate(VI) or **ii)** acidified potassium manganate(VII). This is an important reaction in organic synthesis.



Ethanol — Acidified Dichromate(VI) — Ethanoic Acid



Ethanol — Acidified Manganate(VII) — Ethanoic Acid

Organic Chemistry

Reactions of the Alcohols – Oxidation

- Ethanol is the alcohol found in *alcoholic beverages* such as beer, wine and spirits.

- If a glass of wine is left exposed to the air, oxygen in the air can *oxidise* the ethanol to ethanoic acid, making the wine taste like *vinegar*.

Organic Chemistry

Reactions of the Alcohols – Sodium

- Ethanol reacts with sodium to form a salt and hydrogen.

ethanol + sodium → sodium ethoxide + hydrogen

$2CH_3CH_2OH + 2Na \rightarrow 2Na^+CH_3CH_2O^- + H_2$

Compare: $2H_2O + 2Na \rightarrow 2Na^+ OH^- + H_2$

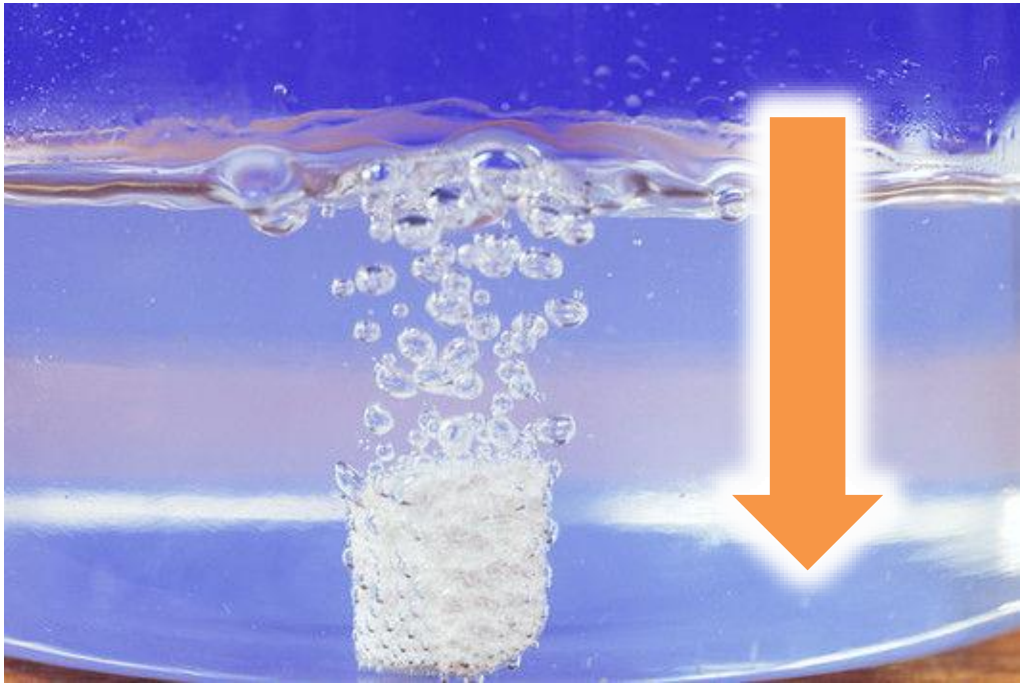
Organic Chemistry

Reactions of the Alcohols – Sodium

- The density of *sodium* = 0.968 g cm^{-3}
- The density of *water* = 1.00 g cm^{-3}
- The density of *ethanol* = 0.789 g cm^{-3}

Organic Chemistry

Reactions of the Alcohols – Sodium



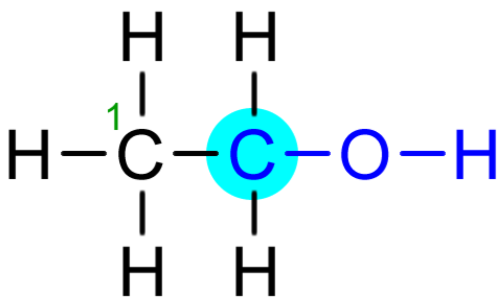
- Consequence: Sodium *floats* on *water*, but *sinks* in *ethanol*.

Organic Chemistry

Enrichment – Primary, Secondary and Tertiary Alcohols

Organic Chemistry

Enrichment – Primary, Secondary and Tertiary Alcohols

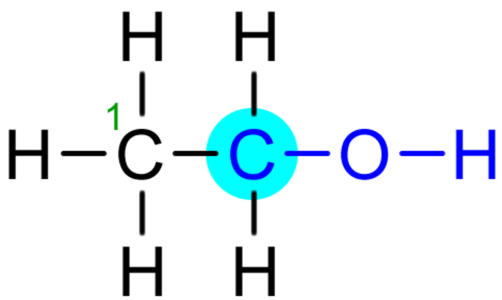


ethanol is
a primary (1°)
alcohol

- For *primary alcohols*, the carbon atom to which the hydroxyl group (–OH) is bonded has only *one* other carbon atom *directly* bonded to it.

Organic Chemistry

Enrichment – Primary, Secondary and Tertiary Alcohols



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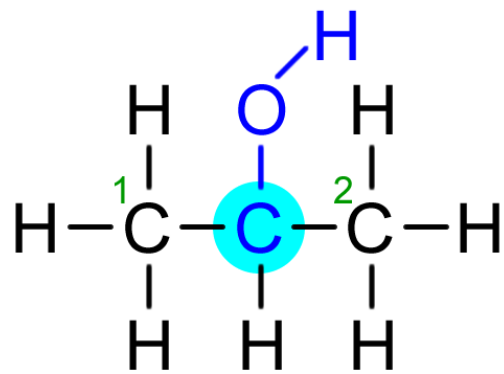
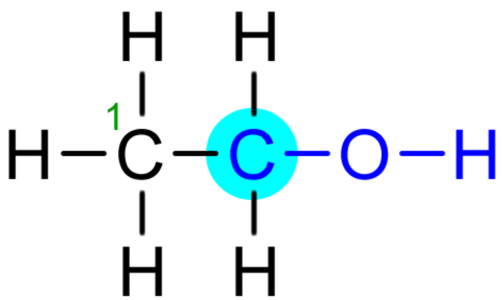


propan-2-ol is
a secondary (2°)
alcohol

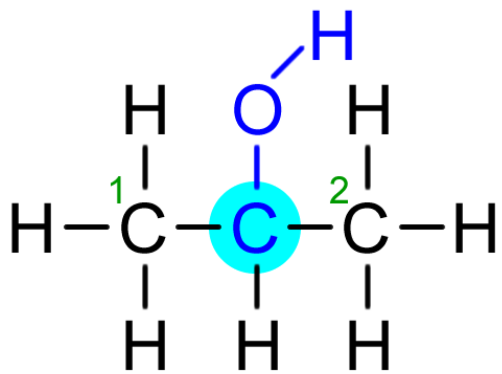
- For *secondary alcohols*, the carbon atom to which the hydroxyl group (–OH) is bonded has *two* other carbon atoms *directly* bonded to it.

Organic Chemistry

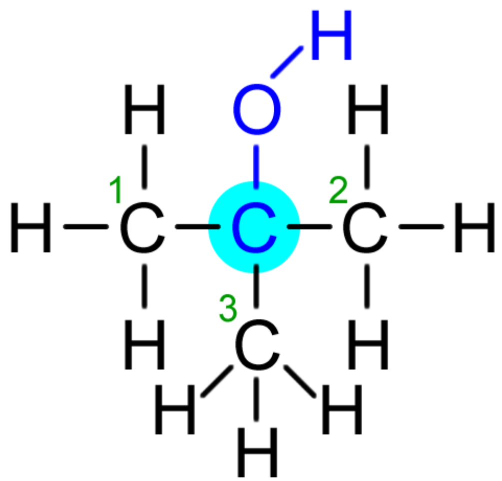
Enrichment – Primary, Secondary and Tertiary Alcohols



ethanol is a primary (1°) alcohol



propan-2-ol is a secondary (2°) alcohol

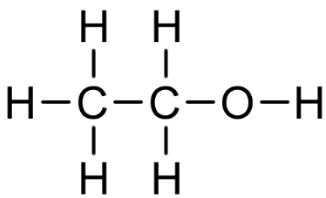


2-methylpropan-2-ol is a tertiary (3°) alcohol

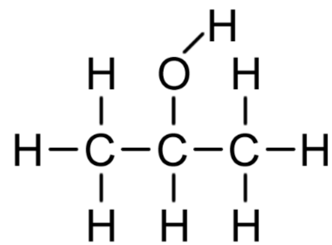
- For *tertiary alcohols*, the carbon atom to which the hydroxyl group (–OH) is bonded has *three* other carbon atoms *directly* bonded to it.

Organic Chemistry

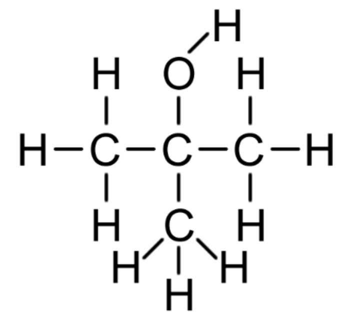
Enrichment – Primary, Secondary and Tertiary Alcohols



primary alcohol
(ethanol)



secondary alcohol
(propan-2-ol)



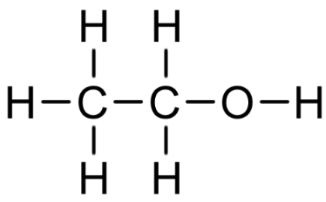
tertiary alcohol
(2-methylpropan-2-ol)

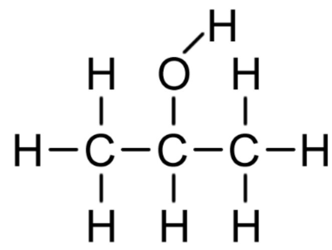
- When warmed with acidified potassium manganate(VII) or acidified potassium dichromate(VI), a *primary alcohol* will be *oxidised* to form an *aldehyde*. The aldehyde can be oxidised further to form a *carboxylic acid*.

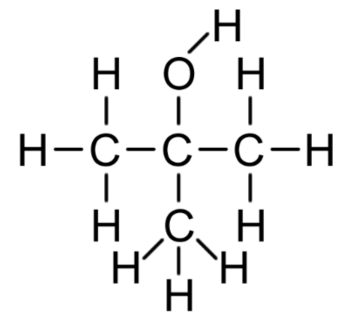
- Note: Acidified potassium manganate(VII) changes from **purple** to **colourless** and acidified potassium dichromate(VI) changes from **orange** to **green**.

Organic Chemistry

Enrichment – Primary, Secondary and Tertiary Alcohols


primary alcohol
(ethanol)


secondary alcohol
(propan-2-ol)

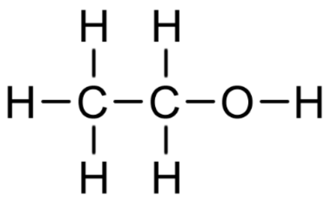

tertiary alcohol
(2-methylpropan-2-ol)

- When warmed with acidified potassium manganate(VII) or acidified potassium dichromate(VI), a *secondary alcohol* will be *oxidised* to form an *ketone*. The ketone *cannot* be oxidised any further.

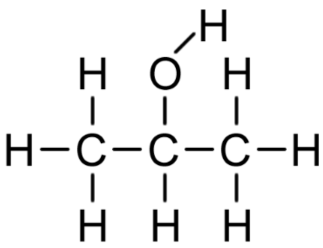
- Note: Acidified potassium manganate(VII) changes from **purple** to **colourless** and acidified potassium dichromate(VI) changes from **orange** to **green**.

Organic Chemistry

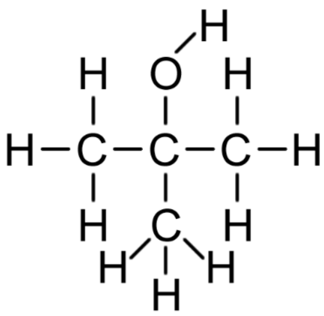
Enrichment – Primary, Secondary and Tertiary Alcohols



primary alcohol
(ethanol)



secondary alcohol
(propan-2-ol)

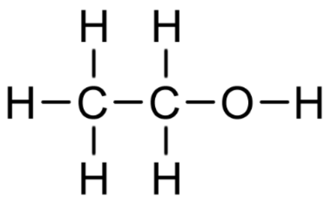


tertiary alcohol
(2-methylpropan-2-ol)

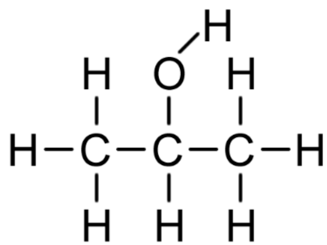
- It is *not* possible to *oxidise tertiary alcohols* by warming them with acidified potassium manganate(VII) or acidified potassium dichromate(VI). There will be no observed reaction / change.

Organic Chemistry

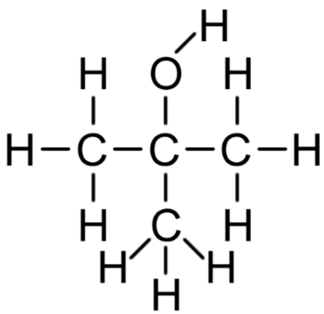
Enrichment – Primary, Secondary and Tertiary Alcohols



primary alcohol
(ethanol)



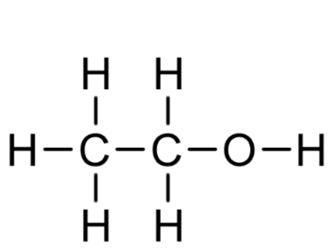
secondary alcohol
(propan-2-ol)



tertiary alcohol
(2-methylpropan-2-ol)

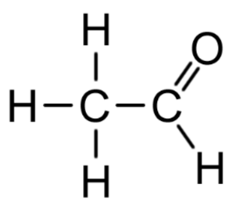
Organic Chemistry

Enrichment – Primary, Secondary and Tertiary Alcohols

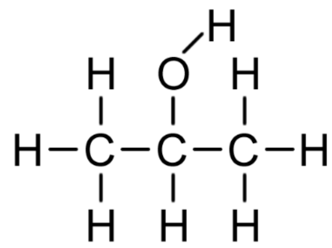


primary alcohol
(ethanol)

$\downarrow$ H_2SO_4 + $KMnO_4$

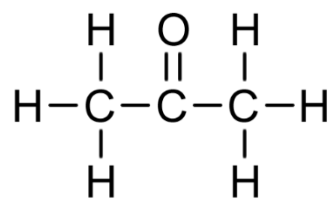


aldehyde (ethanal)

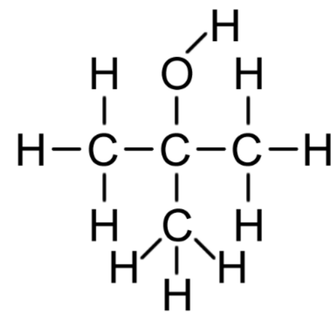


secondary alcohol
(propan-2-ol)

$\downarrow$ H_2SO_4 + $KMnO_4$



ketone (propanone)



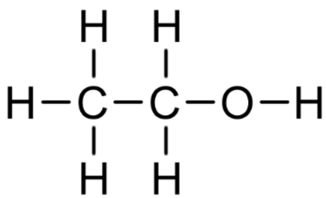
tertiary alcohol
(2-methylpropan-2-ol)

$\downarrow$ H_2SO_4 + $KMnO_4$

tertiary alcohols
are not oxidised
(no observed
reaction / change)

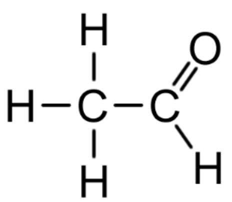
Organic Chemistry

Enrichment – Primary, Secondary and Tertiary Alcohols



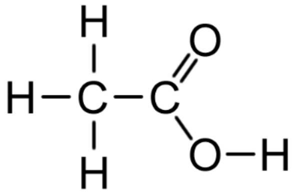
primary alcohol
(ethanol)

↓ H_2SO_4 + $KMnO_4$

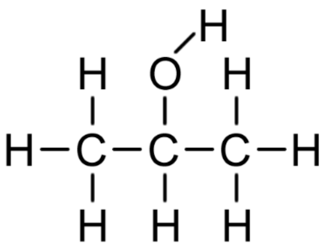


aldehyde (ethanal)

↓ H_2SO_4 + $KMnO_4$

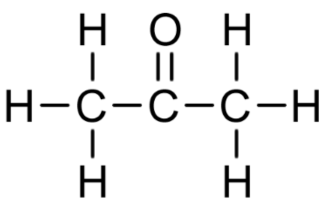


carboxylic acid
(ethanoic acid)



secondary alcohol
(propan-2-ol)

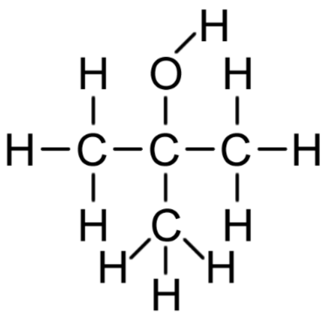
↓ H_2SO_4 + $KMnO_4$



ketone (propanone)

↓ H_2SO_4 + $KMnO_4$

ketones are
not oxidised
(no observed
reaction / change)

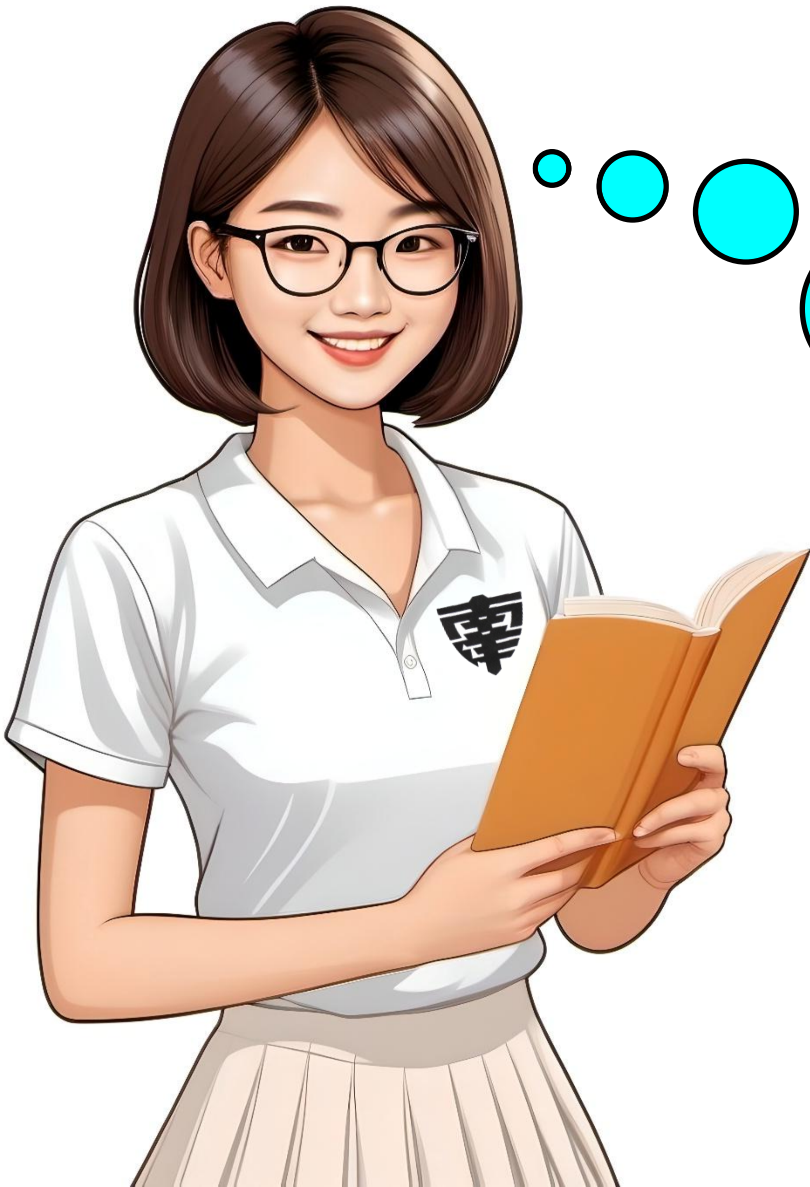


tertiary alcohol
(2-methylpropan-2-ol)

↓ H_2SO_4 + $KMnO_4$

tertiary alcohols
are not oxidised
(no observed
reaction / change)

Organic Chemistry



What are the essential reactions of the *carboxylic acids*?

- Source of $H^+(aq)$
- Esterification

Organic Chemistry

Properties of the Carboxylic Acids

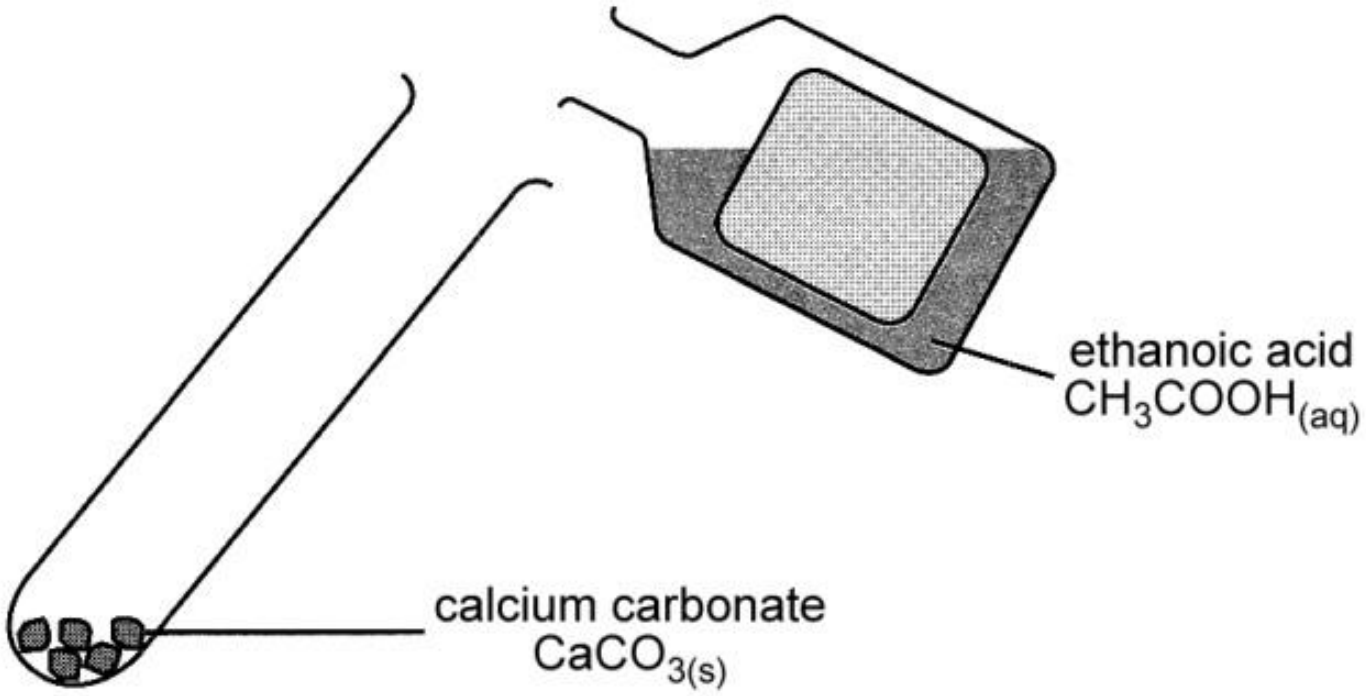
- Remember, carboxylic acids are *weak acids*. This means that they *only partially ionize* when dissolved in water to produce hydrogen ions (H^+) as the only positive ion.

- The reactions of carboxylic acids tend to be *slower* than the reactions of mineral acids of the same concentration. Even though the acids are the same concentration, the carboxylic acid contains a *lower concentration of hydrogen ions*, which will result in a *lower frequency of effective collisions*.

Organic Chemistry

Reactions of the Carboxylic Acids

Carboxylic acids react with carbonates and hydrogen carbonates to form a salt, water and carbon dioxide. This can be used as a qualitative test for a carboxylic acid.



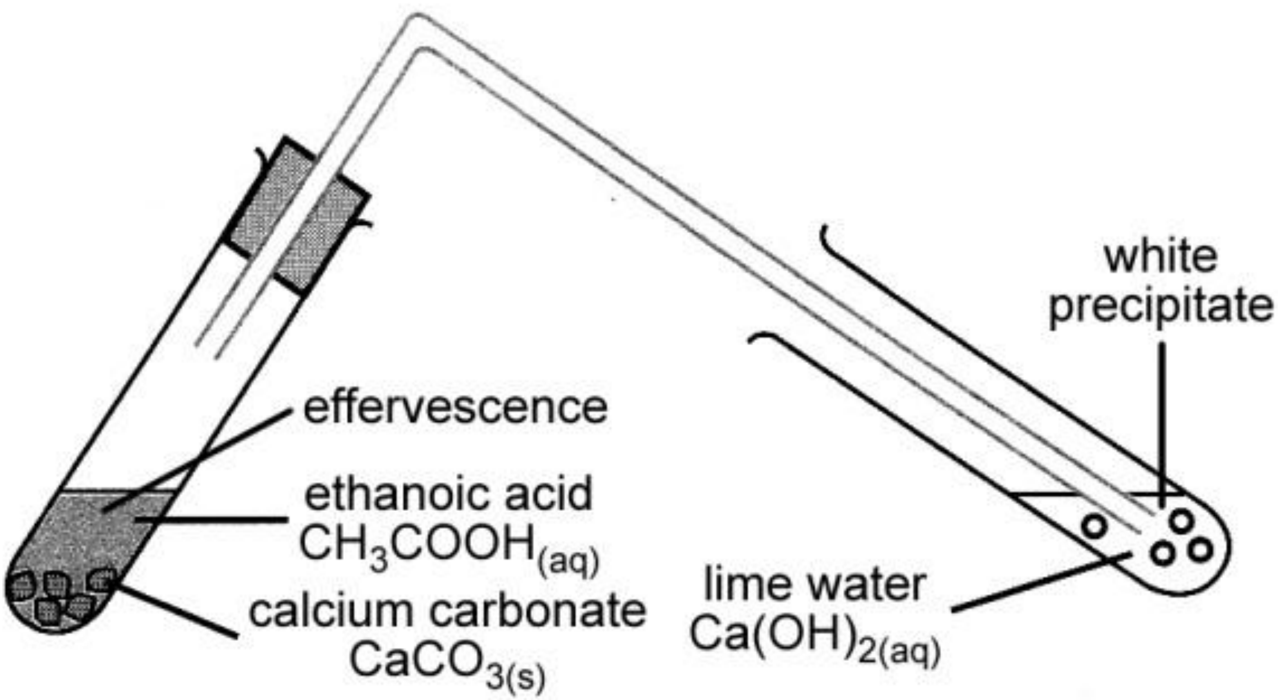
Organic Chemistry

Reactions of the Carboxylic Acids

Acid + Carbonate → Salt + Water + Carbon Dioxide

ethanoic acid + calcium carbonate → calcium ethanoate + water + carbon dioxide

$$2CH_3COOH(aq) + CaCO_3(s) \rightarrow Ca(CH_3COO)_2(aq) + H_2O(l) + CO_2(g)$$



Organic Chemistry

Reactions of the Carboxylic Acids

Acid + Metal $\rightarrow$ Salt + Hydrogen

ethanoic acid + magnesium $\rightarrow$ magnesium ethanoate + hydrogen

$$2CH_3COOH(aq) + Mg(s) \rightarrow Mg(CH_3COO)_2(aq) + H_2(g)$$

Acid + Alkali / Base $\rightarrow$ Salt + Water

ethanoic acid + sodium hydroxide $\rightarrow$ sodium ethanoate + water

$$CH_3COOH(aq) + NaOH(aq) \rightarrow NaCH_3COO(aq) + H_2O(l)$$

Organic Chemistry

Reactions of the Carboxylic Acids

- *Esterification* is the general name for a chemical reaction in which a carboxylic acid and an alcohol react to form an ester and water. Concentrated sulfuric acid is used as the catalyst.

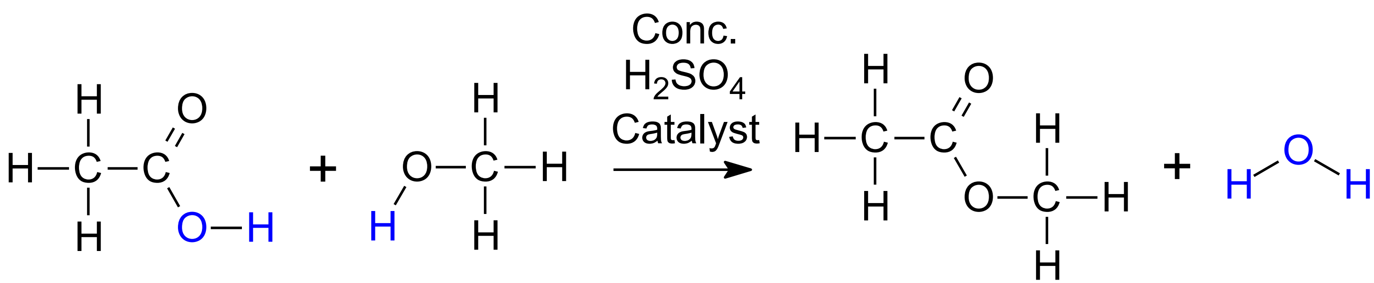
$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

- The reaction is known as a *condensation reaction* because water is produced as one of the products.
- The reaction is reversible and the percentage yield of the ester can be increased by using *Le Chatelier's Principle*, *e.g.* use excess alcohol and remove the ester from the reaction vessel.
- Esters often have a *pleasant*, *fruity odor*. This leads to their extensive use in the fragrance and flavor industry. Ester bonds are also found in many *polymers*.

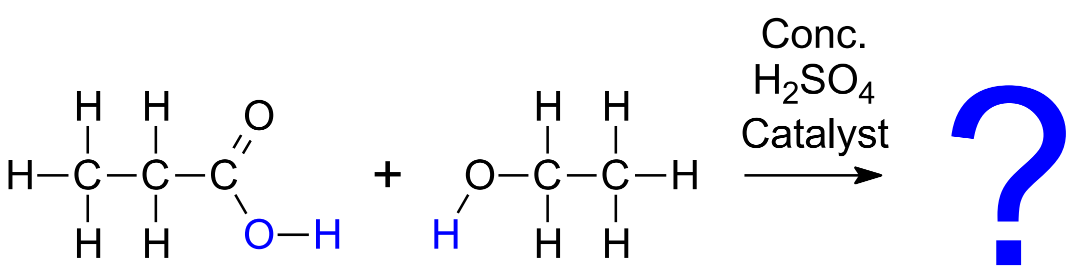
Organic Chemistry

Reactions of the Carboxylic Acids – Esterification

Esters are have a sweet aroma and are used in the food and perfume industry.



Ethanoic Acid | Methanol | Methyl Ethanoate | Water

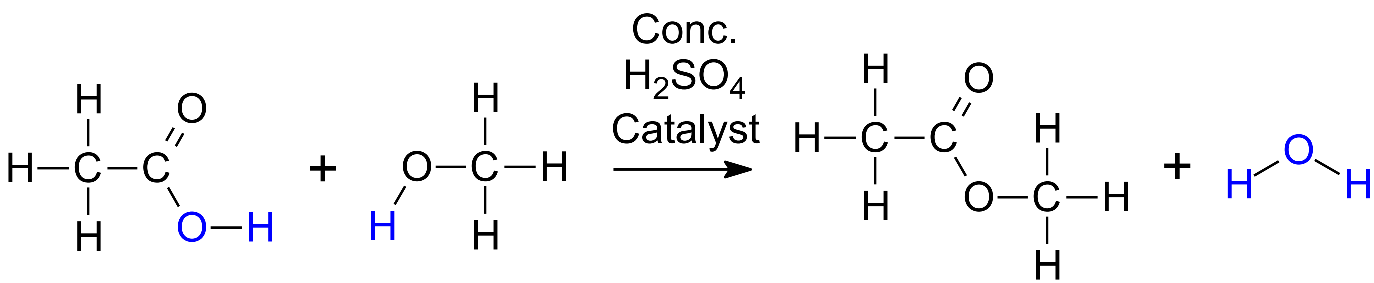


Propanoic Acid | Ethanol

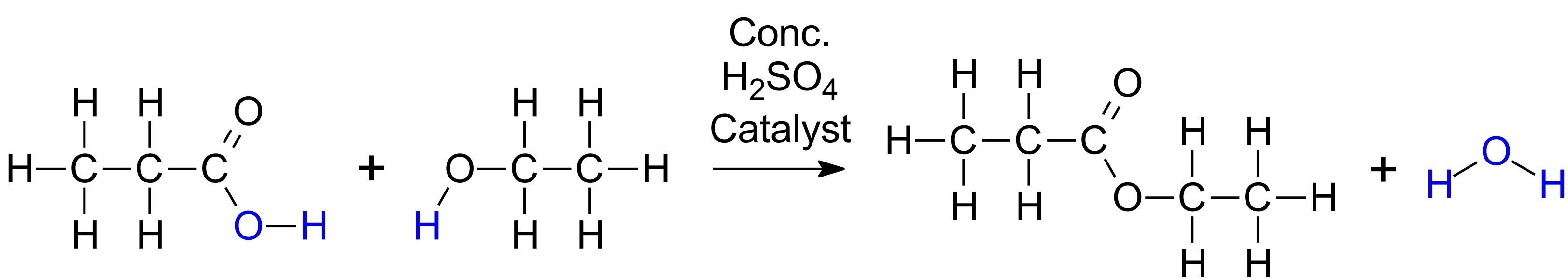
Organic Chemistry

Reactions of the Carboxylic Acids – Esterification

Esters are have a sweet aroma and are used in the food and perfume industry.



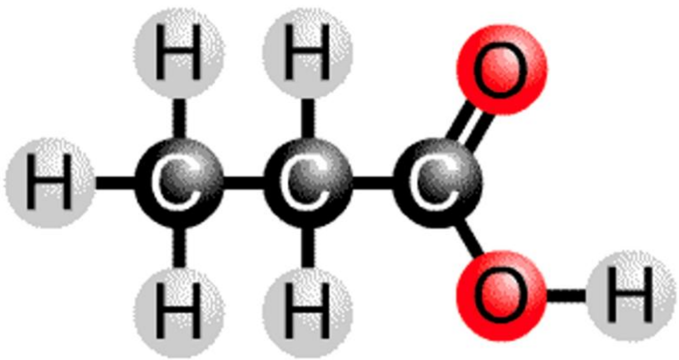
Ethanoic Acid + Methanol → Methyl Ethanoate + Water

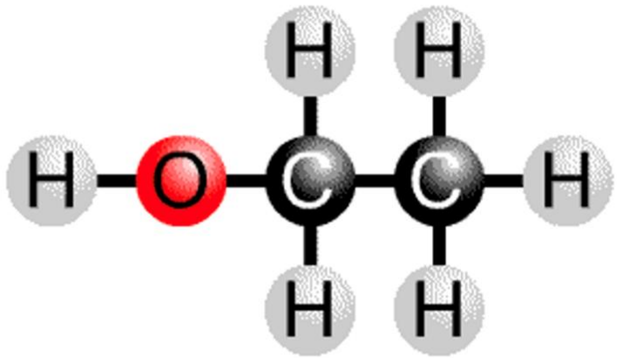


Propanoic Acid + Ethanol → Ethyl Propanoate + Water

Organic Chemistry

Reactions of the Carboxylic Acids – Esterification



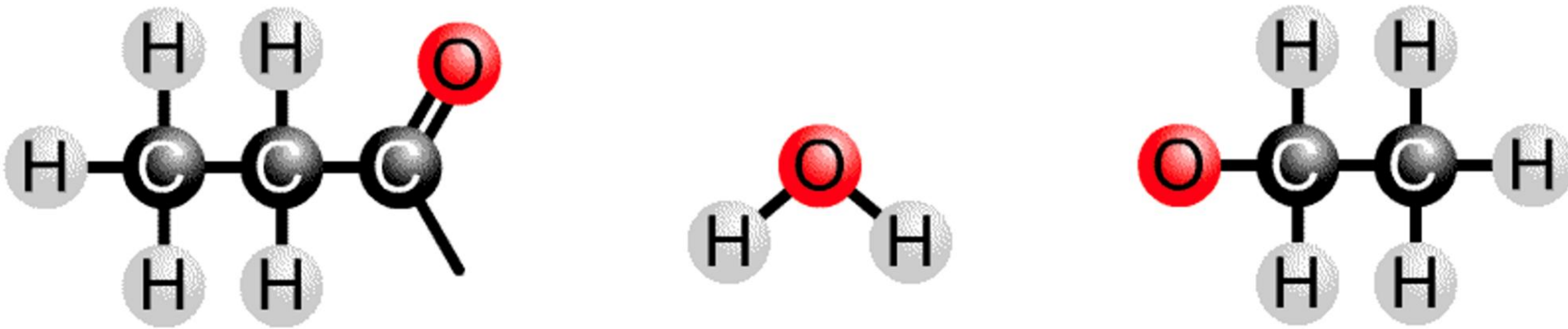


propanoic acid + ethanol → ethyl propanoate + water

$$C_2H_5COOH\ (l) + C_2H_5OH\ (l) \rightarrow C_2H_5COOC_2H_5\ (l) + H_2O\ (l)$$

Organic Chemistry

Reactions of the Carboxylic Acids – Esterification



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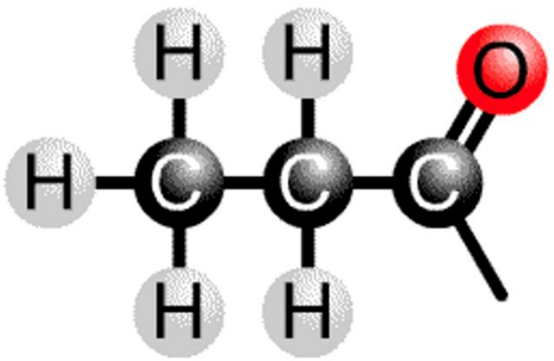
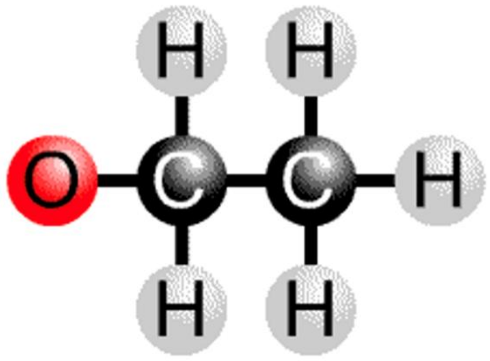
Organic Chemistry

Reactions of the Carboxylic Acids – Esterification





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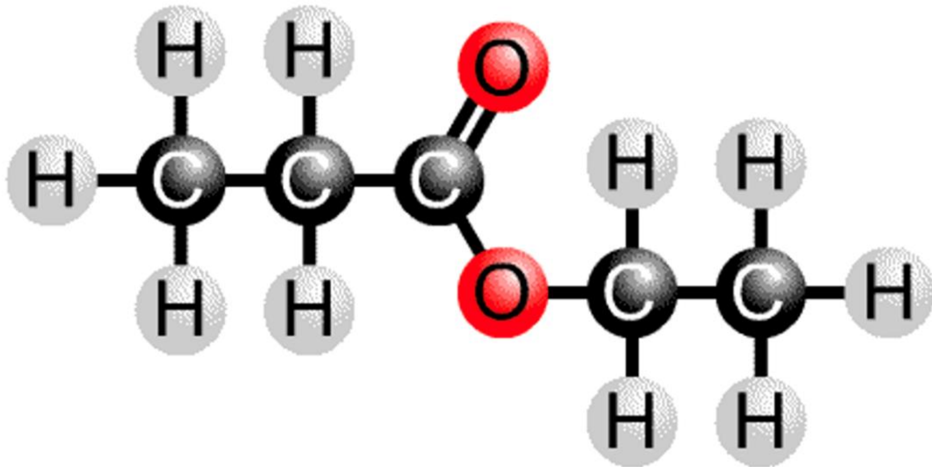
Organic Chemistry

Reactions of the Carboxylic Acids – Esterification

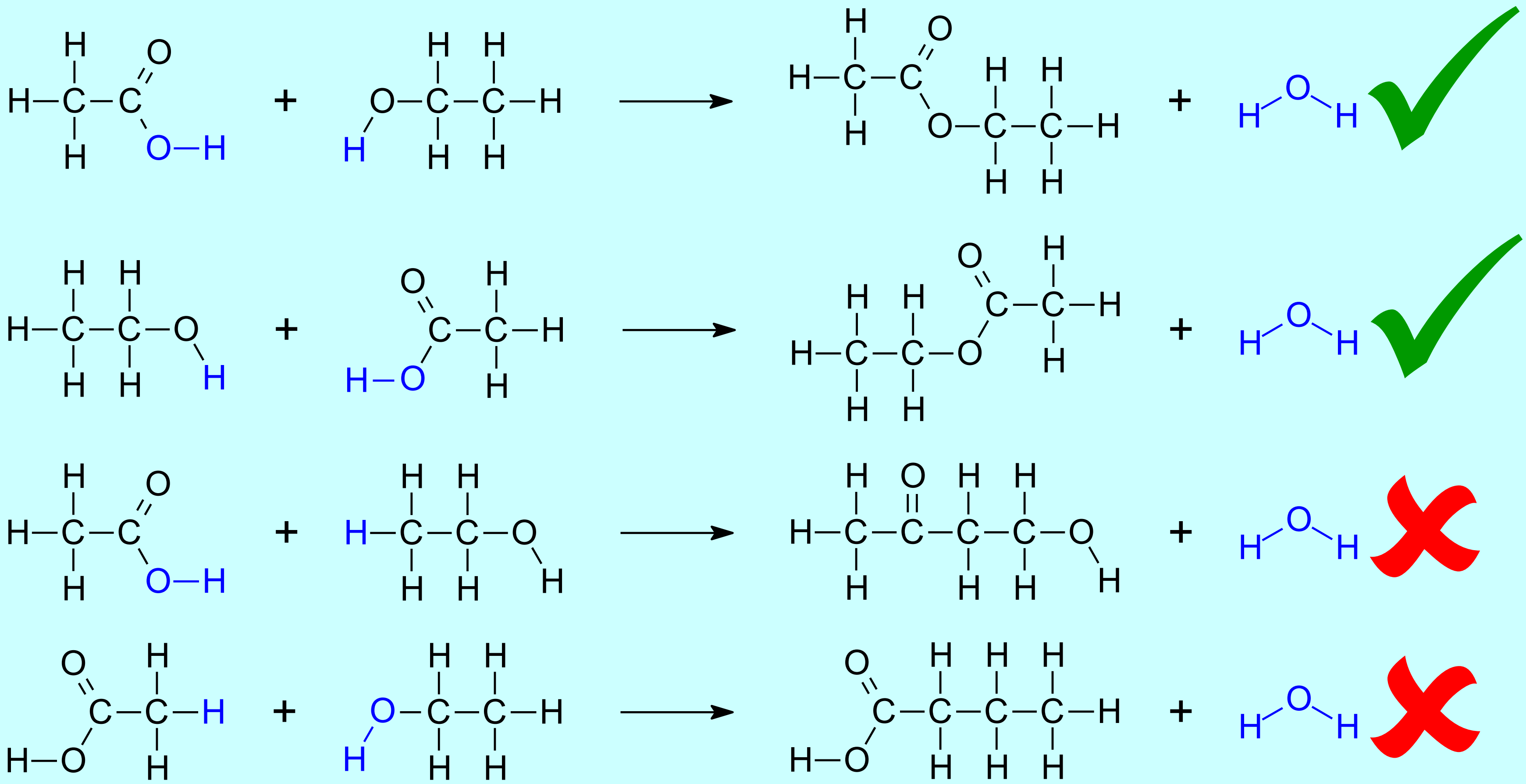


propanoic acid + ethanol $\rightarrow$ ethyl propanoate + water

$C_2H_5COOH\ (l) + C_2H_5OH\ (l) \rightarrow C_2H_5COOC_2H_5\ (l) + H_2O\ (l)$

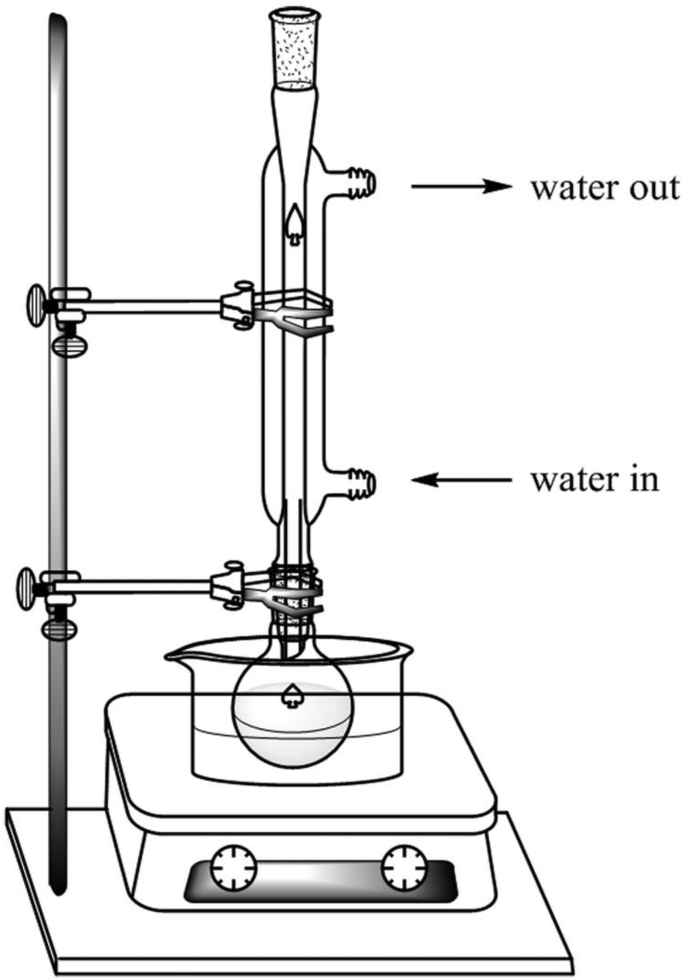
Organic Chemistry

Reactions of the Carboxylic Acids – Esterification



Organic Chemistry

Reactions of the Carboxylic Acids – Esterification



- The carboxylic acid and alcohol are heated under *reflux* in the presence of a *catalyst* (a few drops of concentrated sulfuric acid).

- The condenser prevents volatile organic chemicals escaping from the reaction flask.

Organic Chemistry

Reactions of the Carboxylic Acids – Esterification

- Esters have a pleasant, sweet, fruity aroma.

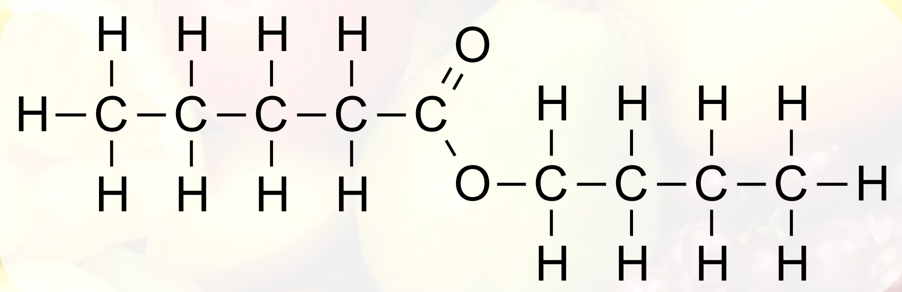
- Esters occur naturally in fruits and are used in the food industry and in perfumery.

Organic Chemistry

Reactions of the Carboxylic Acids – Esterification

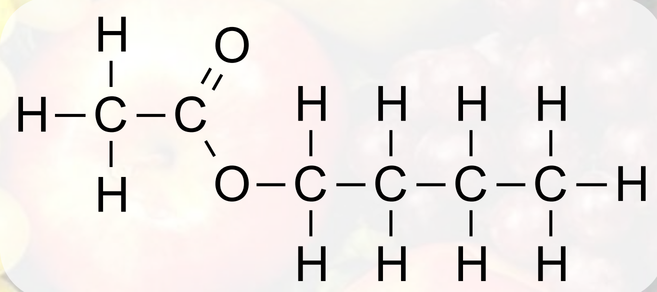
Organic Chemistry

Reactions of the Carboxylic Acids – Esterification



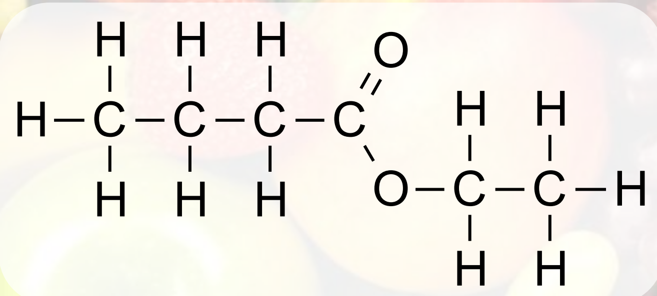
Butyl Pentanoate

Pineapple



Butyl Ethanoate

Apple



Ethyl Butanoate

Banana
Pineapple
Strawberry

Organic Chemistry

Reactions of the Carboxylic Acids – Esterification

Organic Chemistry

Reactions of the Carboxylic Acids – Esterification

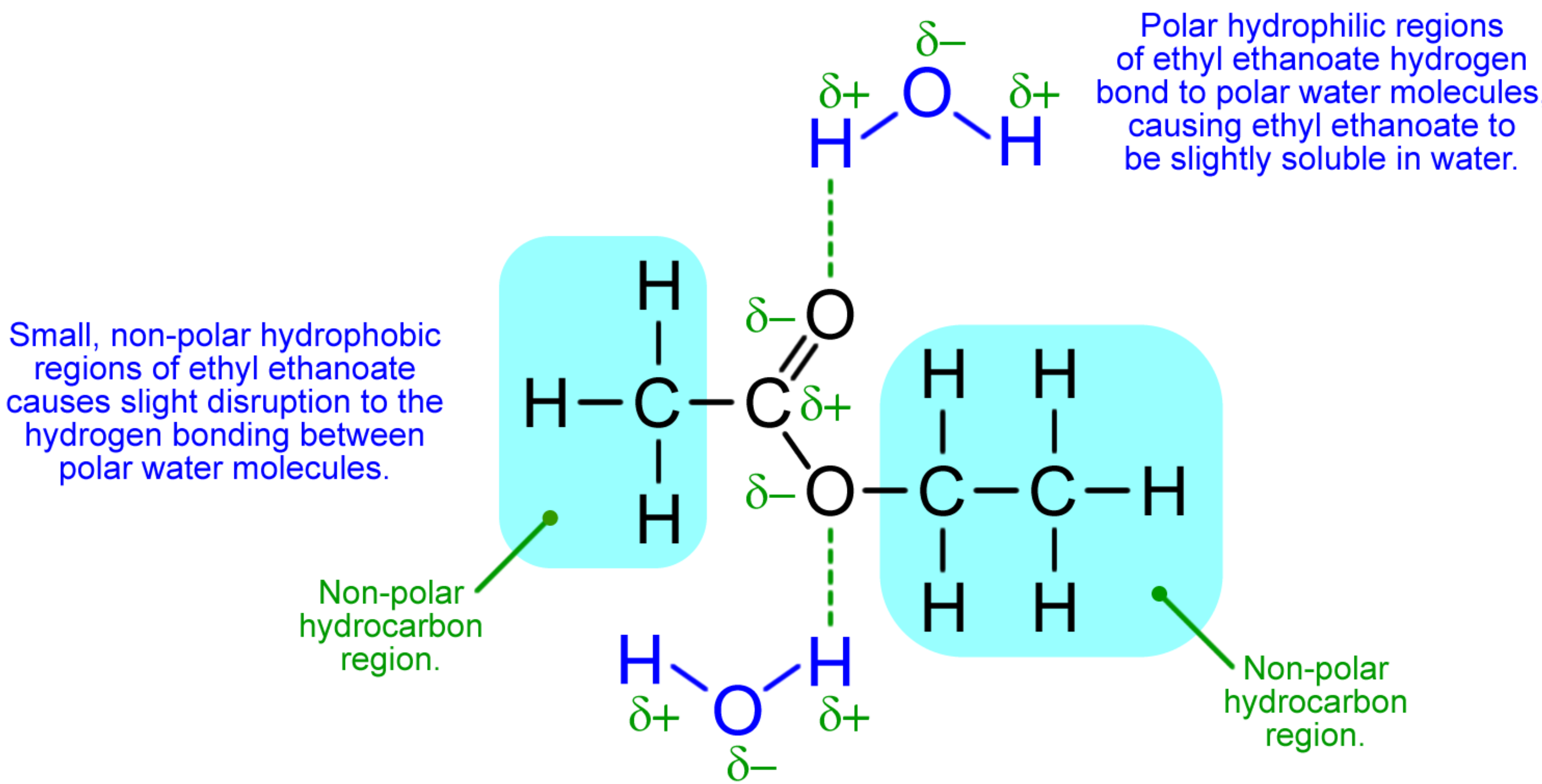
- Esters that have a low relative molecular mass tend to be *volatile liquids* at room temperature and pressure. For example, ethyl ethanoate (M_r = 88.0) boils at 77.1 °C.

- Esters with a low relative molecular mass are reasonably good *solvents* for non-polar compounds, and are commonly employed as solvents in certain types of paint, varnish, glue and nail polish.

- For example, once liquid nail polish has been applied, the volatile ester used as the solvent (usually ethyl ethanoate) readily evaporates, causing the nail polish to dry and harden.

Organic Chemistry

Reactions of the Carboxylic Acids – Esterification



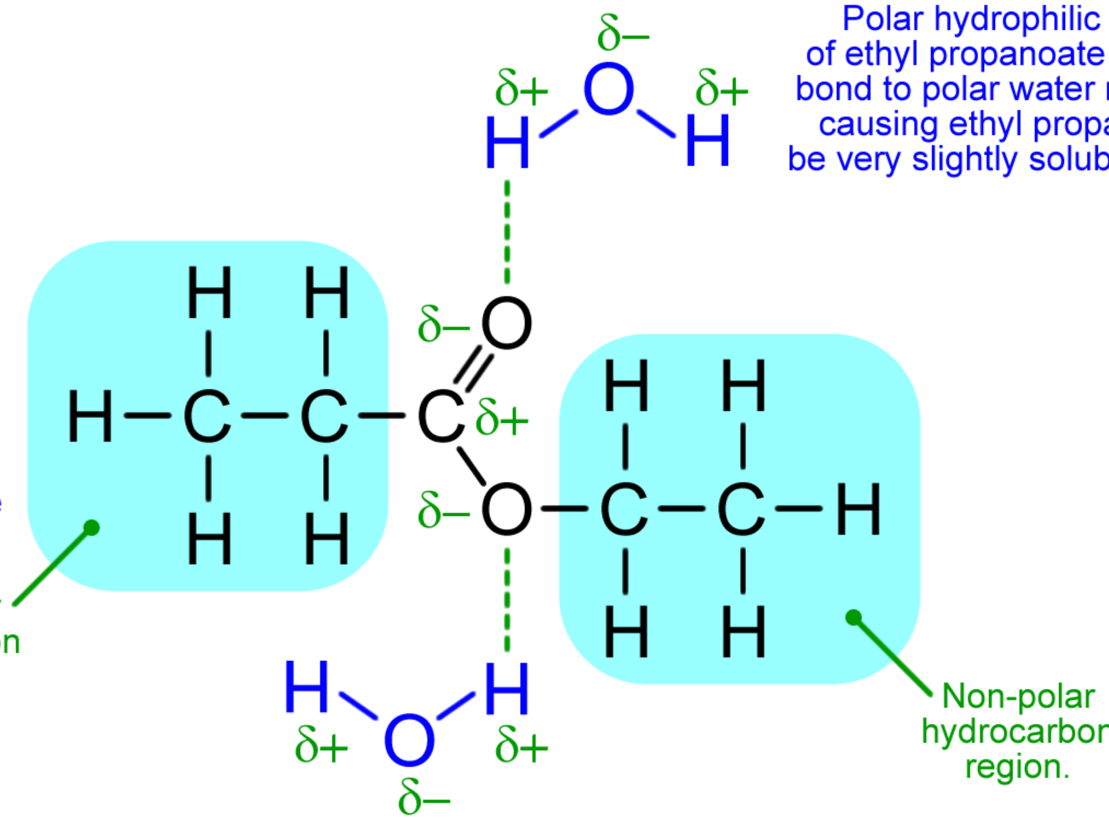
- The solubility of *ethyl ethanoate* in water at room temperature is *8.70 g* of ester per 100 g of water.

Organic Chemistry

Reactions of the Carboxylic Acids – Esterification

Polar hydrophilic regions of ethyl propanoate hydrogen bond to polar water molecules, causing ethyl propanoate to be very slightly soluble in water.

Non-polar hydrophobic regions of ethyl propanoate cause significant disruption to the hydrogen bonding between polar water molecules, reducing the solubility of ethyl propanoate in water.



- The solubility of *ethyl propanoate* in water at room temperature is *1.70 g* of ester per 100 g of water.

Organic Chemistry

Reactions of the Carboxylic Acids – Esterification

- Esters are polar molecules, but are unable to form ester ↔ ester hydrogen bonds. Consequently, only weak intermolecular forces of attraction – or London dispersion forces – exist between ester molecules, so their melting points and boiling points are significantly lower than those of a carboxylic acid composed of the same number of carbon atoms and with a similar relative molecular mass.

Organic Chemistry

Reactions of the Carboxylic Acids – Esterification

- Although esters cannot hydrogen bond with each other, they can hydrogen bond with water molecules.

- A hydrogen atom carrying a slight positive charge ($\delta+$) in a water molecule can form a hydrogen bond with an oxygen atom carrying a slight negative charge ($\delta-$) in the ester, $\delta+$ H - - - O $\delta-$.

- Because of this, esters with a low relative molecular mass, and short hydrocarbon chains, are slightly miscible / soluble with water.

Organic Chemistry

Reactions of the Carboxylic Acids – Esterification

- The formation of hydrogen bonds between the ester molecules and water molecules releases some of the energy that is required to hydrate / solvate the ester.

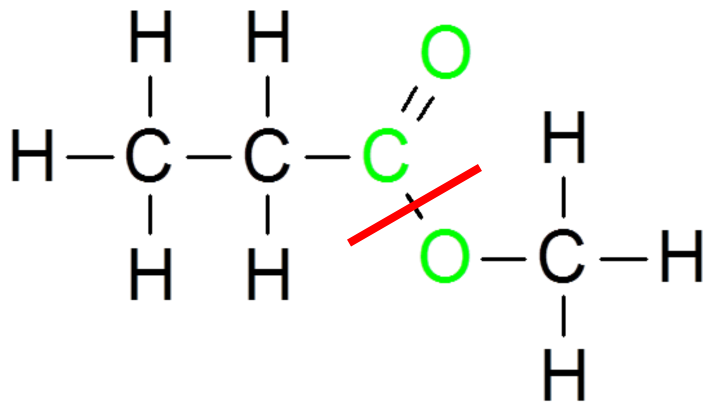
- However, as the length of the non-polar hydrocarbon chains increases, it causes greater disruption to the relatively strong hydrogen bonds between the water molecules, a process that is energetically unfavourable.

- As a consequence, as relative molecular mass increases, and hydrocarbon chain-length increases, the solubility of an ester in water decreases.

Organic Chemistry

Reactions of the Carboxylic Acids – Ester Hydrolysis

- Esters can be *hydrolysed* (broken down by water) to form the original carboxylic acid and alcohol. Warm with dilute acid or alkali.



Step 1: Break the C–O bond that is attached to the C=O group.

Step 2: Draw the fragments that are produced after the C–O bond has been broken.

Organic Chemistry

Reactions of the Carboxylic Acids – Ester Hydrolysis

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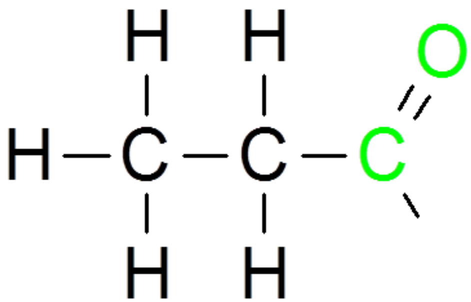

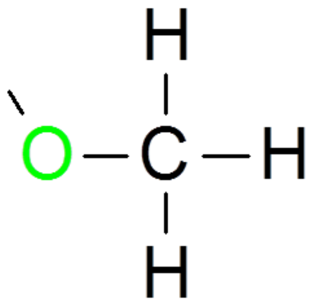

Step 3: Add water, H_2O, to the fragments that are formed.

→ O–H is bonded to the C=O group. This completes the carboxylic acid functional group, *–COOH*.

→ H is bonded to the single O. This completes the alcohol functional group, *–OH*.

Organic Chemistry

Reactions of the Carboxylic Acids – Ester Hydrolysis

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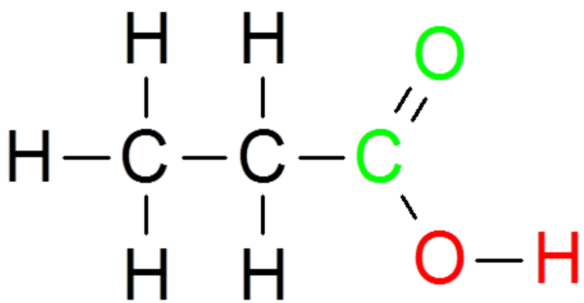
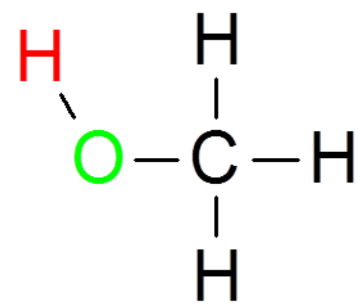


Propanoic Acid

Methanol



Step 3: Add water, H_2O, to the fragments that are formed.

→ O–H is bonded to the C=O group. This completes the carboxylic acid functional group, *–COOH*.

→ H is bonded to the single O. This completes the alcohol functional group, *–OH*.

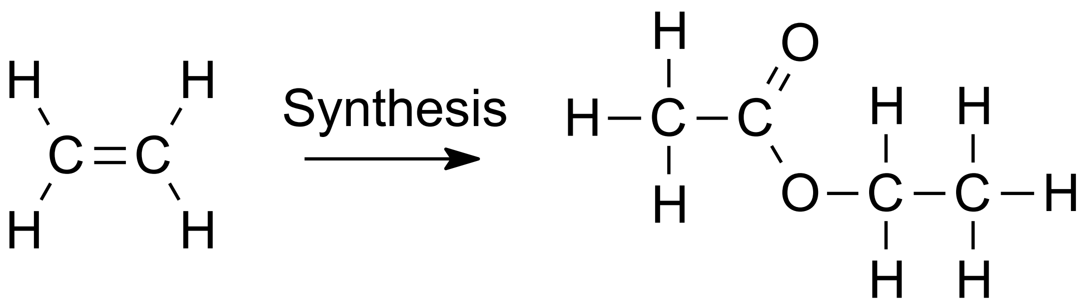
Organic Chemistry

How would you synthesise the ester *ethyl ethanoate* from the alkene *ethene*?

Organic Chemistry

Synthetic Pathway

The synthesis of useful organic compounds from relatively small and simple starting materials is one of the main objectives of an organic chemist. For example, how would you synthesise the sweet smelling ester, ethyl ethanoate, from ethene?

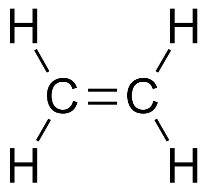


Ethene

Ethyl Ethanoate

Organic Chemistry

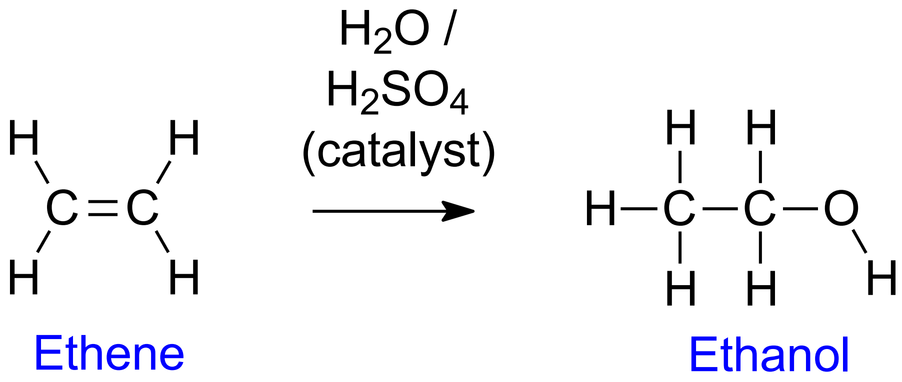
Synthetic Pathway



Ethene

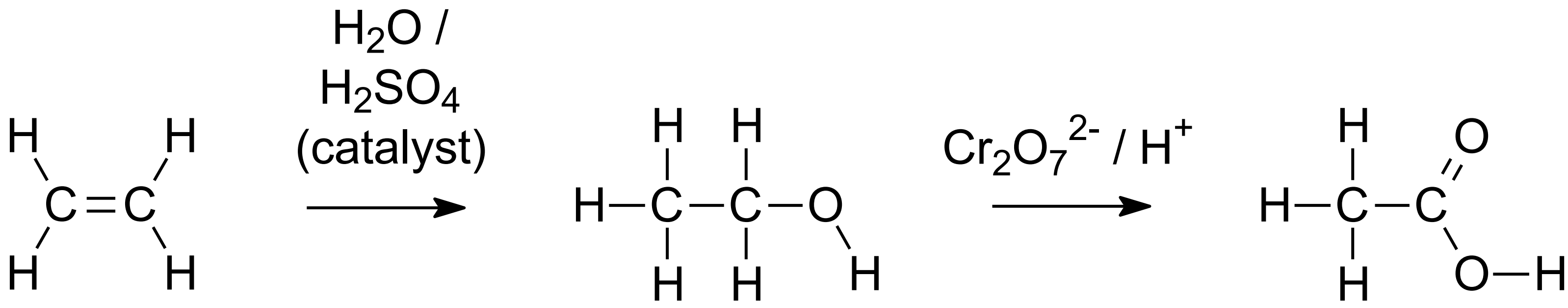
Organic Chemistry

Synthetic Pathway



Organic Chemistry

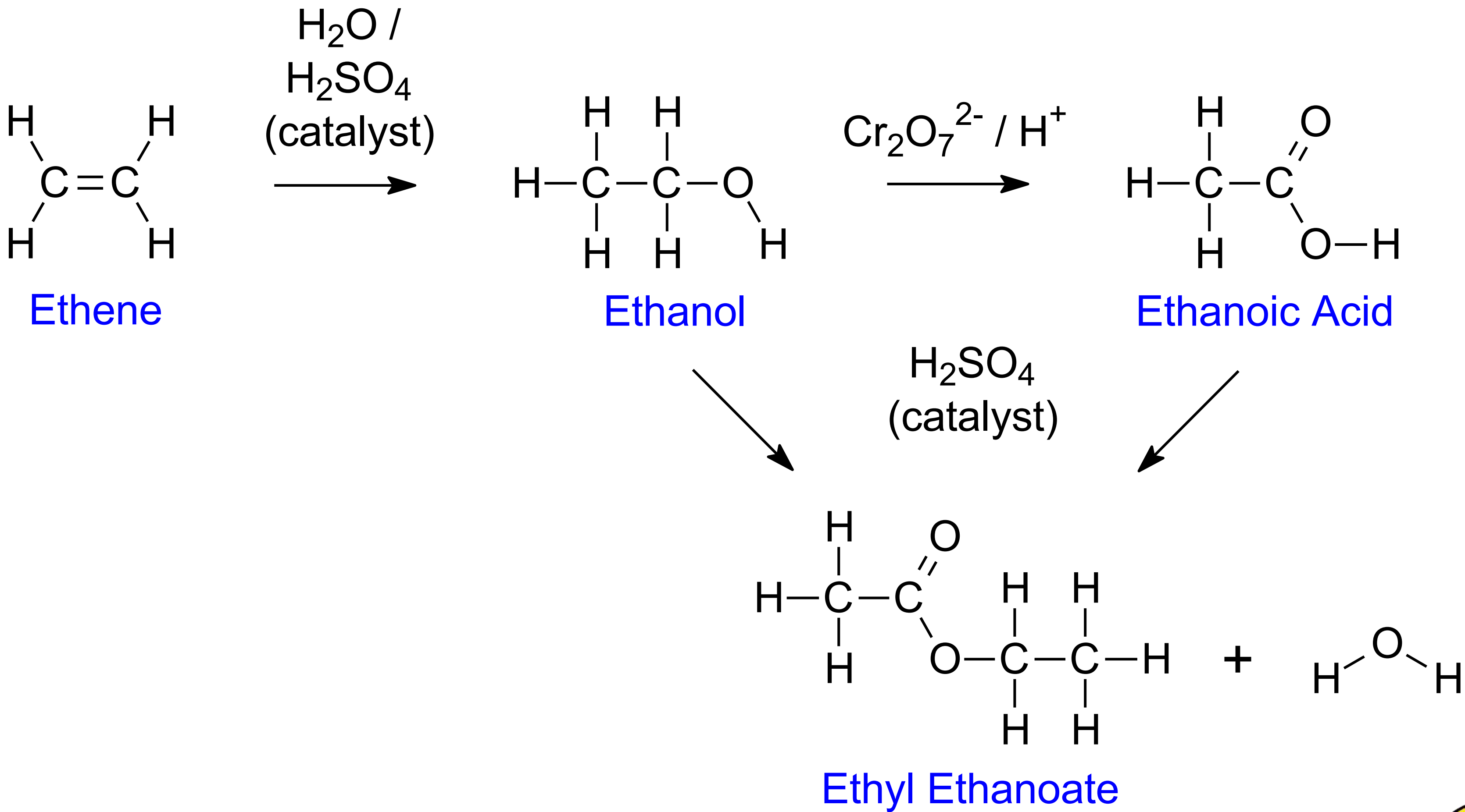
Synthetic Pathway



Ethene Ethanol Ethanoic Acid

Organic Chemistry

Synthetic Pathway



Organic Chemistry

Organic Chemistry

Summary: Reactions of Organic Compounds

Alkanes
C_nH_{2n+2}

Carboxylic Acids
$C_nH_{2n}O_2$

Alkenes
C_nH_{2n}

Esters
$C_nH_{2n}O_2$

Halogenoalkanes
$C_nH_{2n+1}Hal$

Alcohols
$C_nH_{2n+1}OH$

Organic Chemistry

Summary: Reactions of Organic Compounds

Alkanes
C_nH_{2n+2}

Carboxylic Acids
$C_nH_{2n}O_2$

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C_nH_{2n}

Esters
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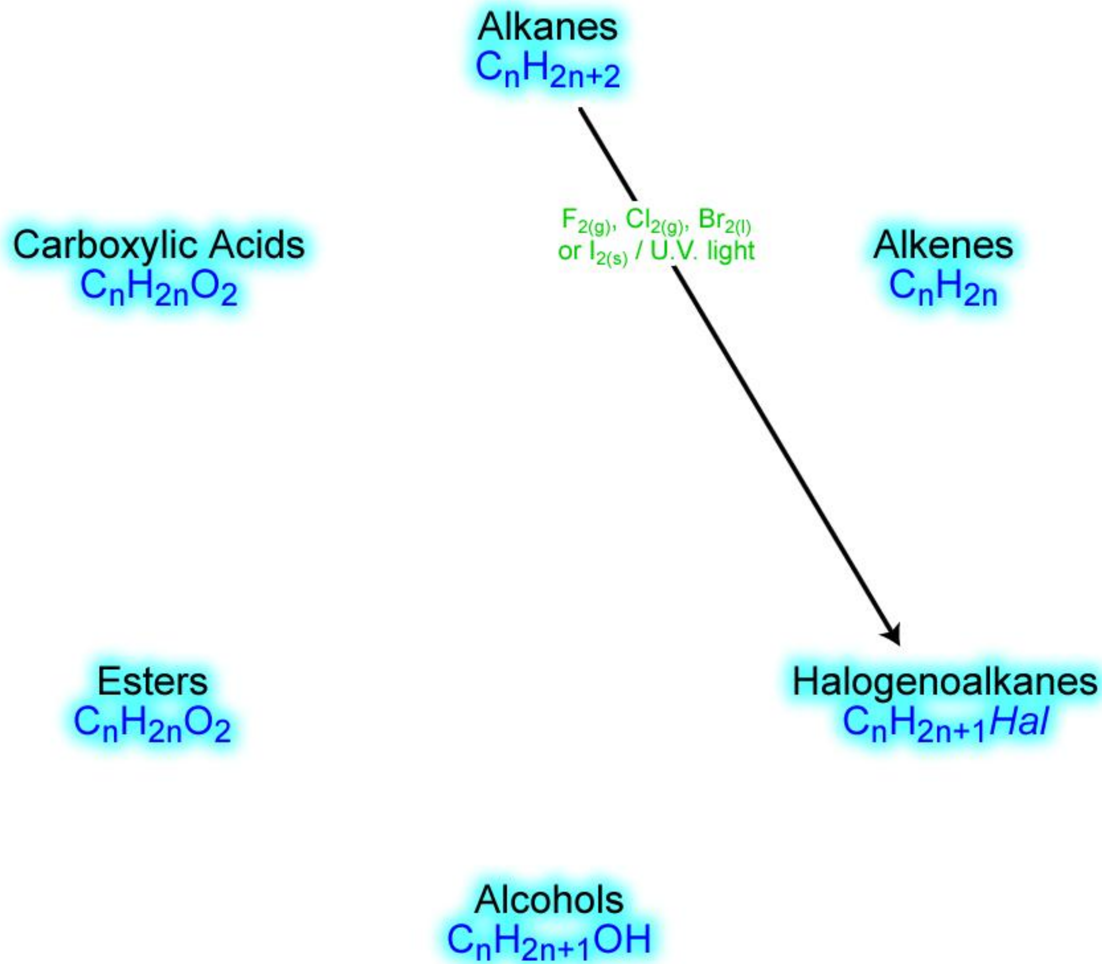
$C_nH_{2n+1}\mathit{Hal}$

Alcohols
$C_nH_{2n+1}OH$

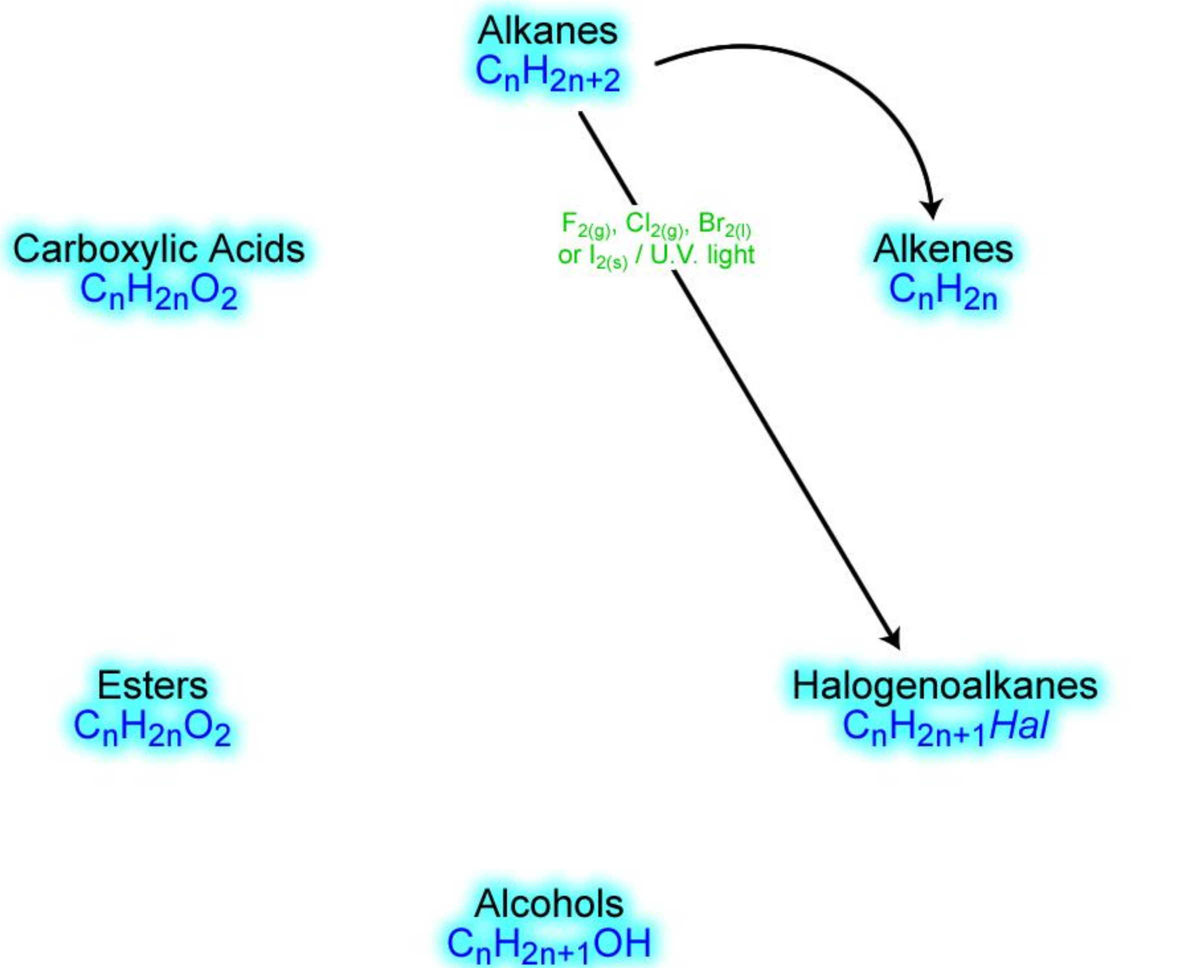
Organic Chemistry

Summary: Reactions of Organic Compounds



Organic Chemistry

Summary: Reactions of Organic Compounds



Organic Chemistry

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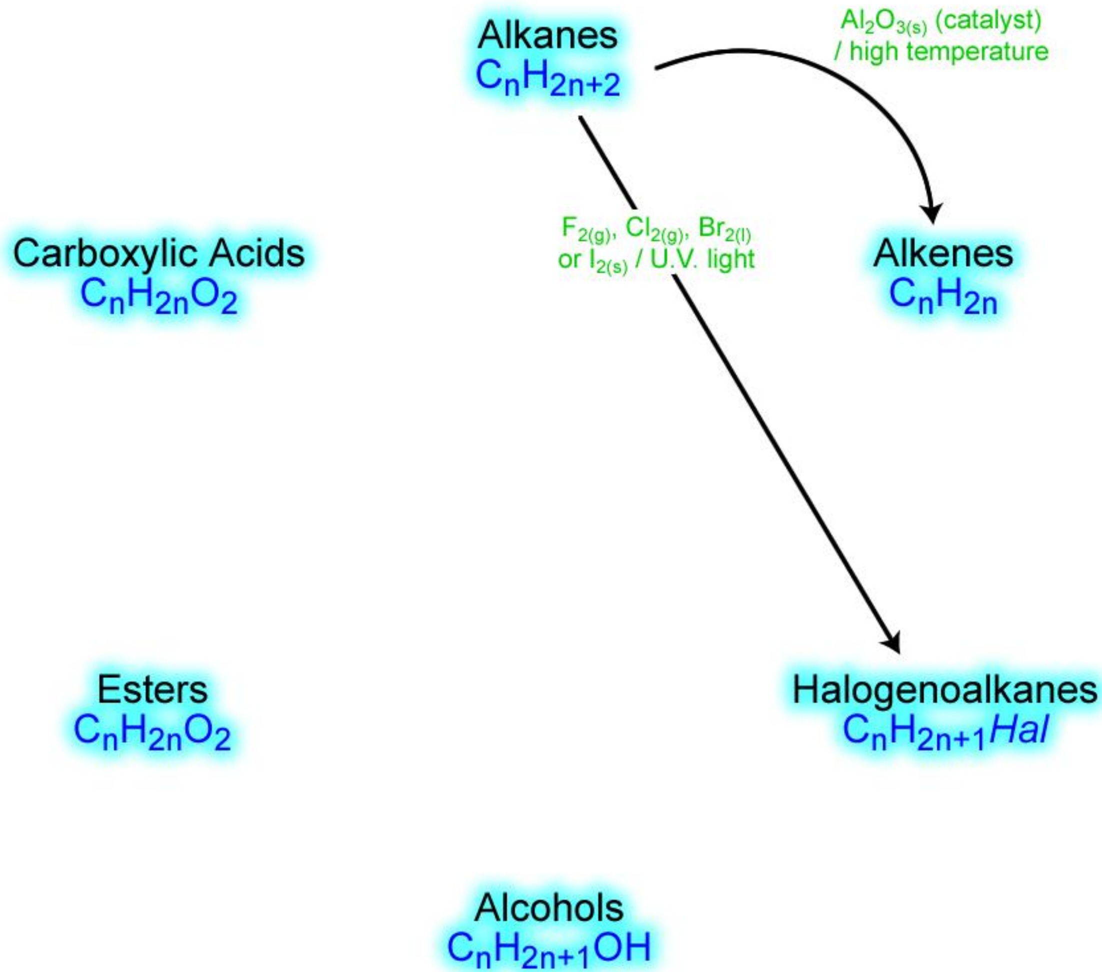

Organic Chemistry

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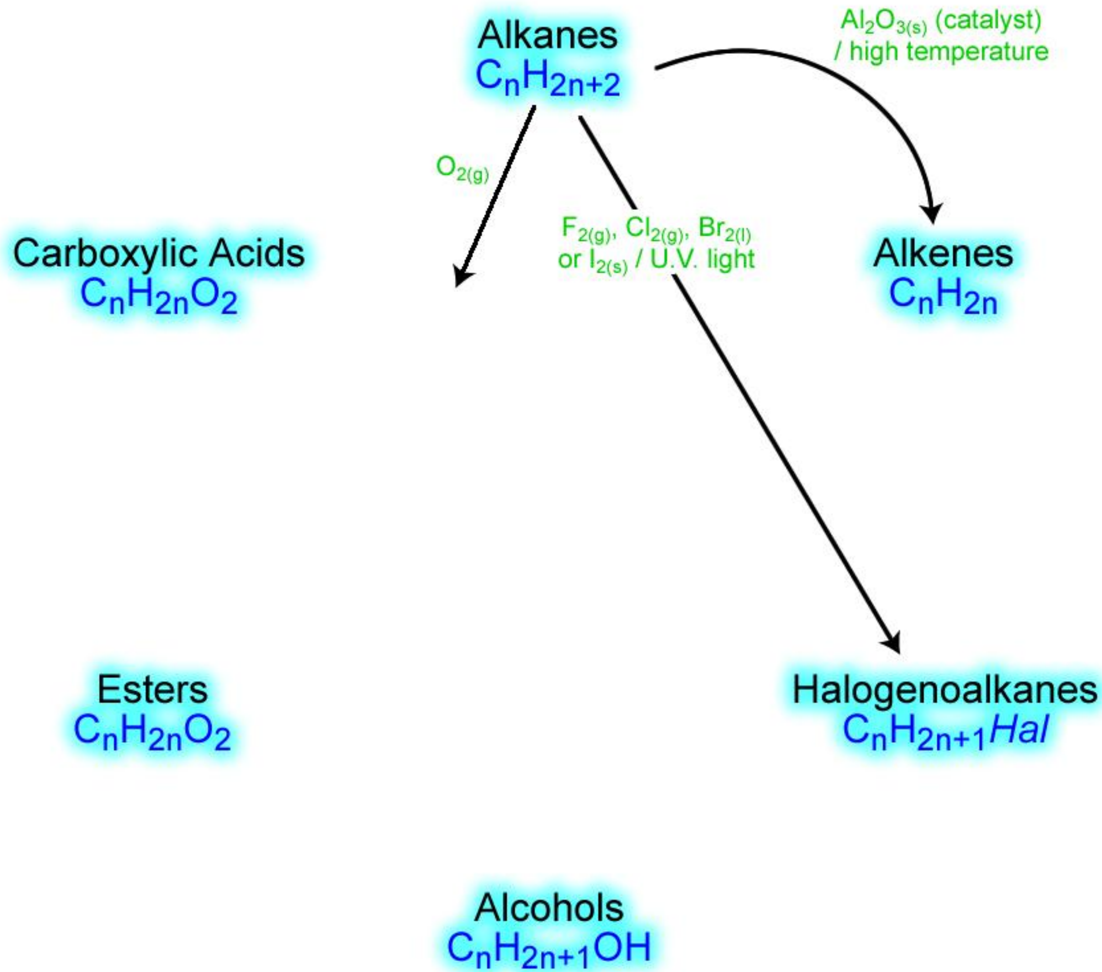

Organic Chemistry

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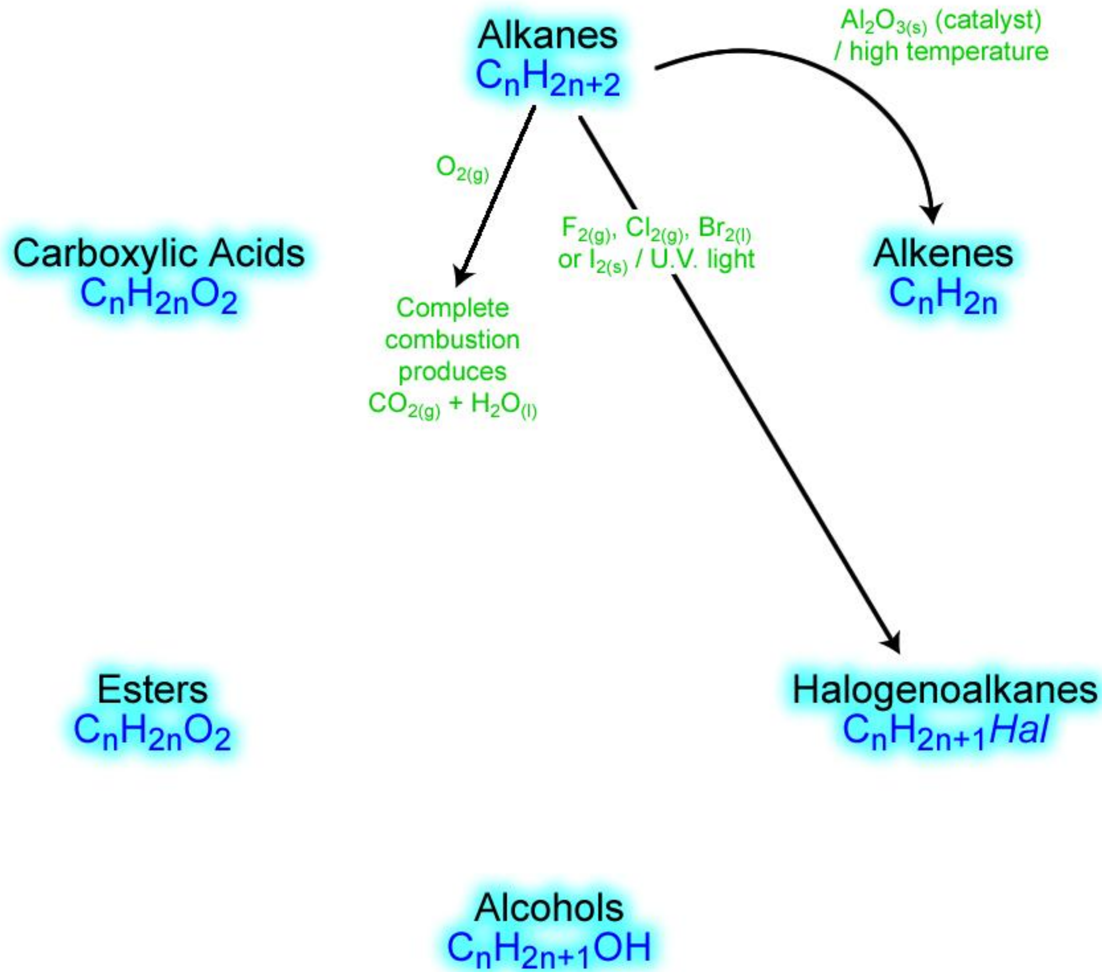
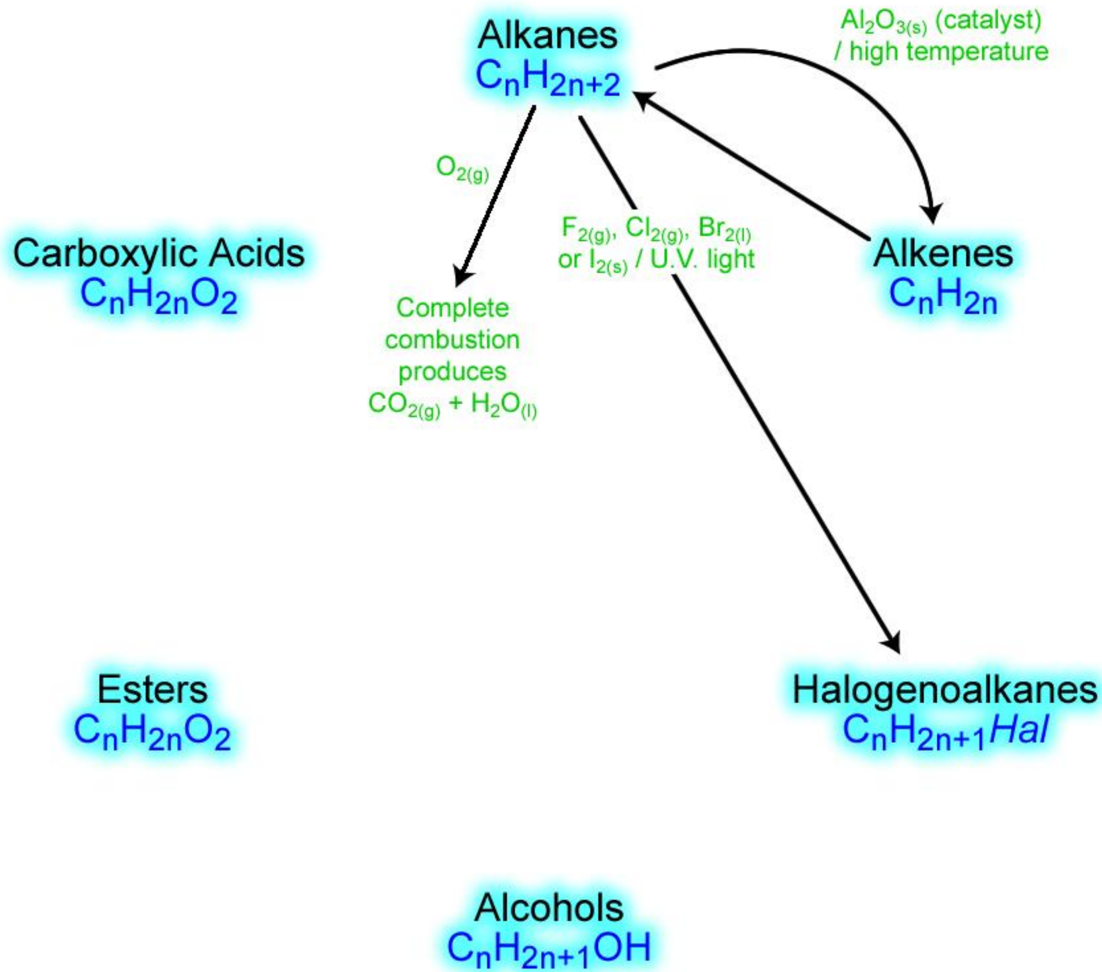


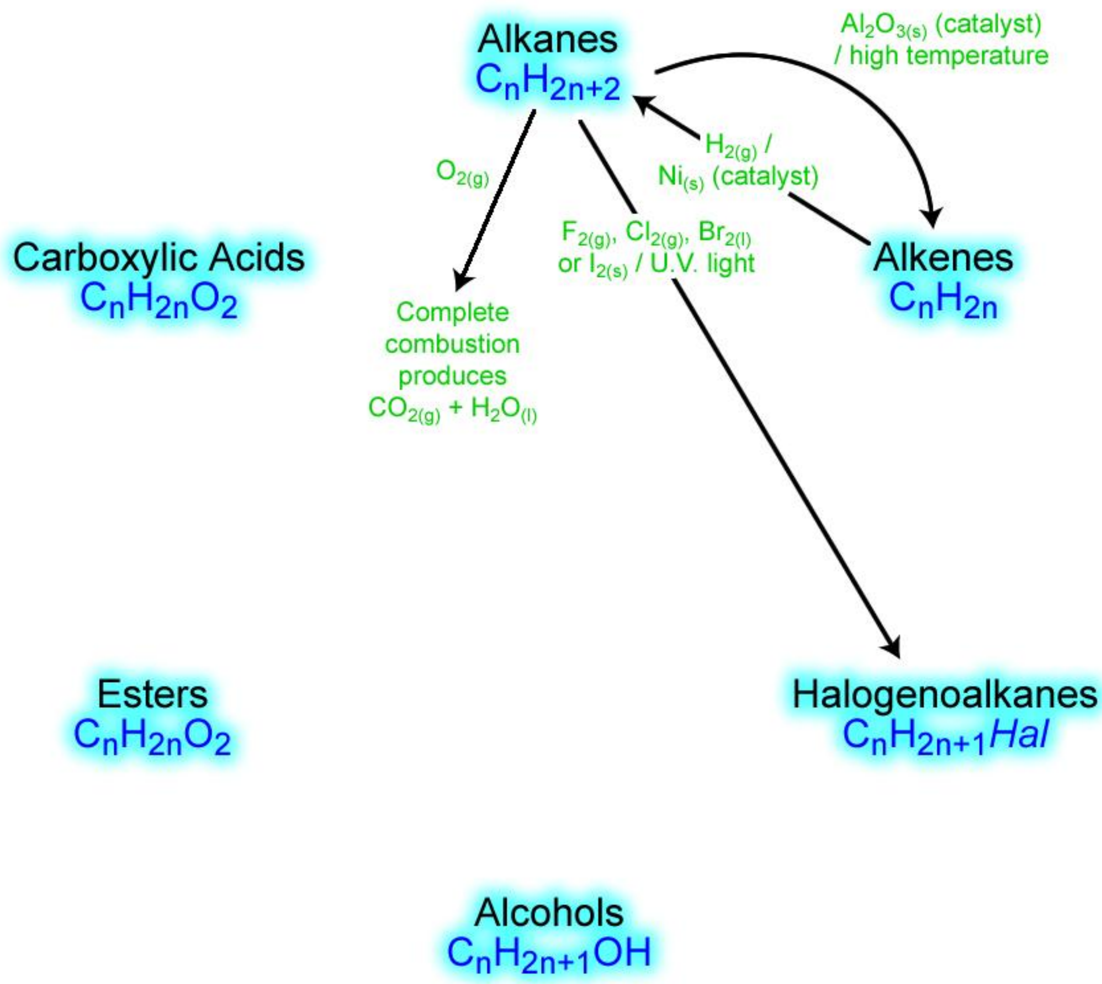
Organic Chemistry

Summary: Reactions of Organic Compounds



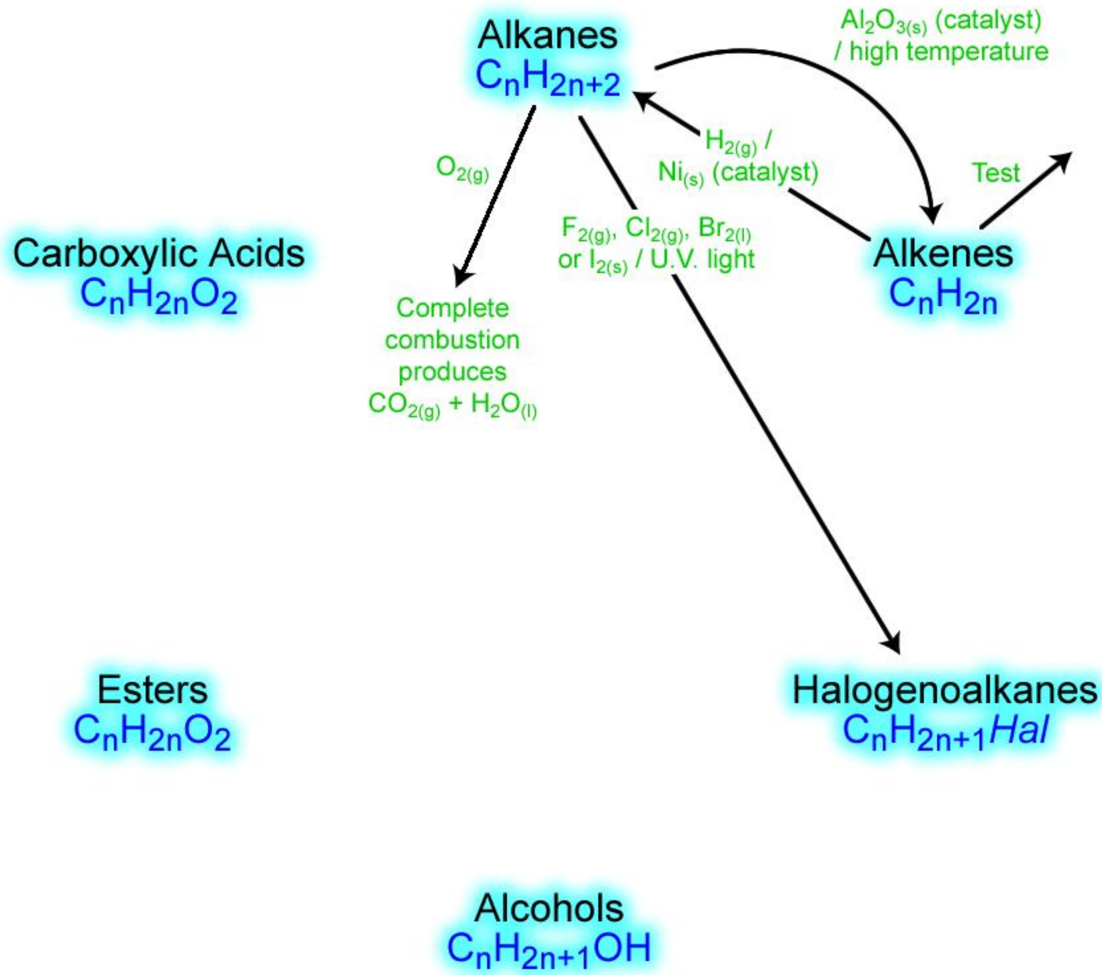
Organic Chemistry

Summary: Reactions of Organic Compounds



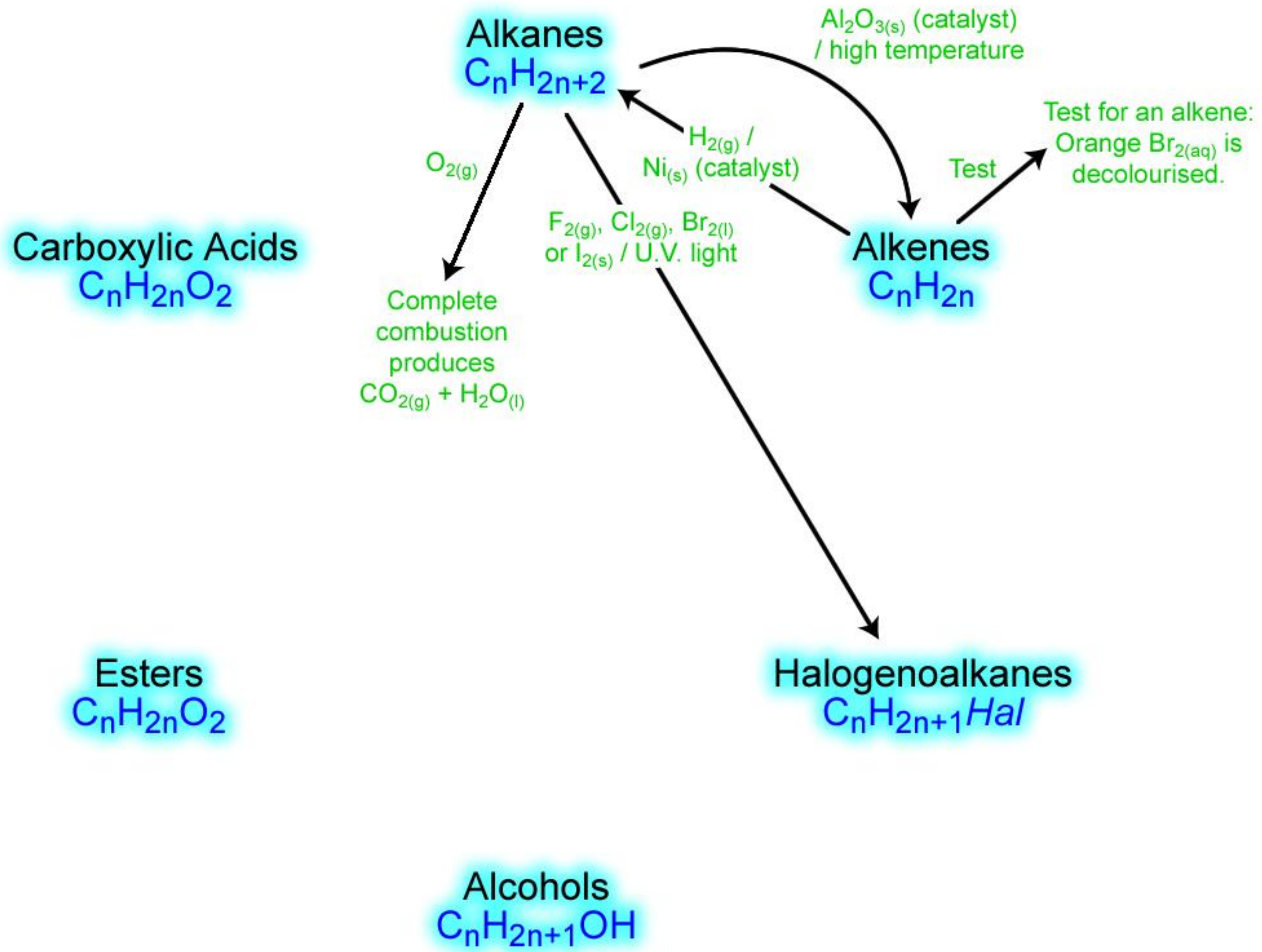
Organic Chemistry

Summary: Reactions of Organic Compounds



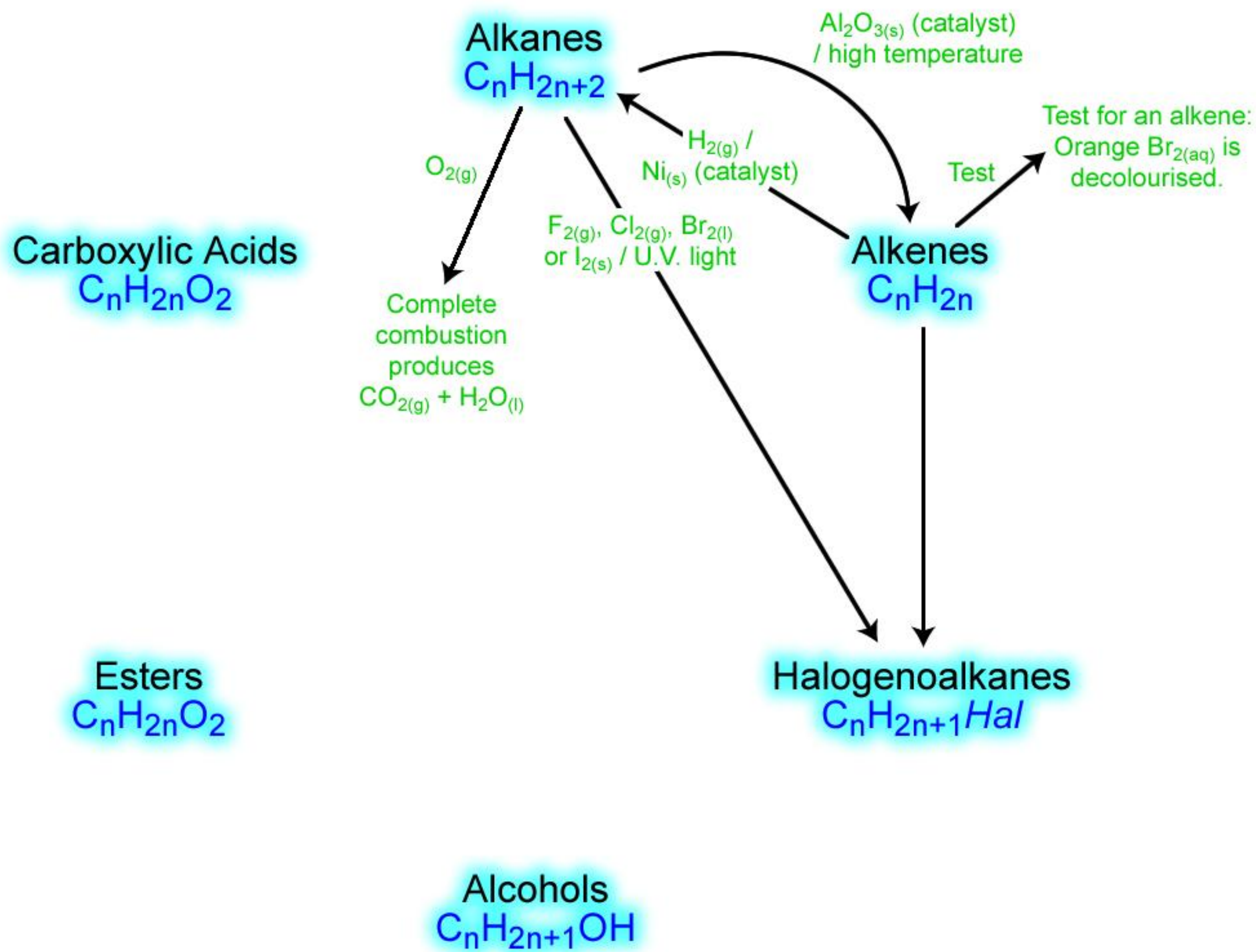
Organic Chemistry

Summary: Reactions of Organic Compounds



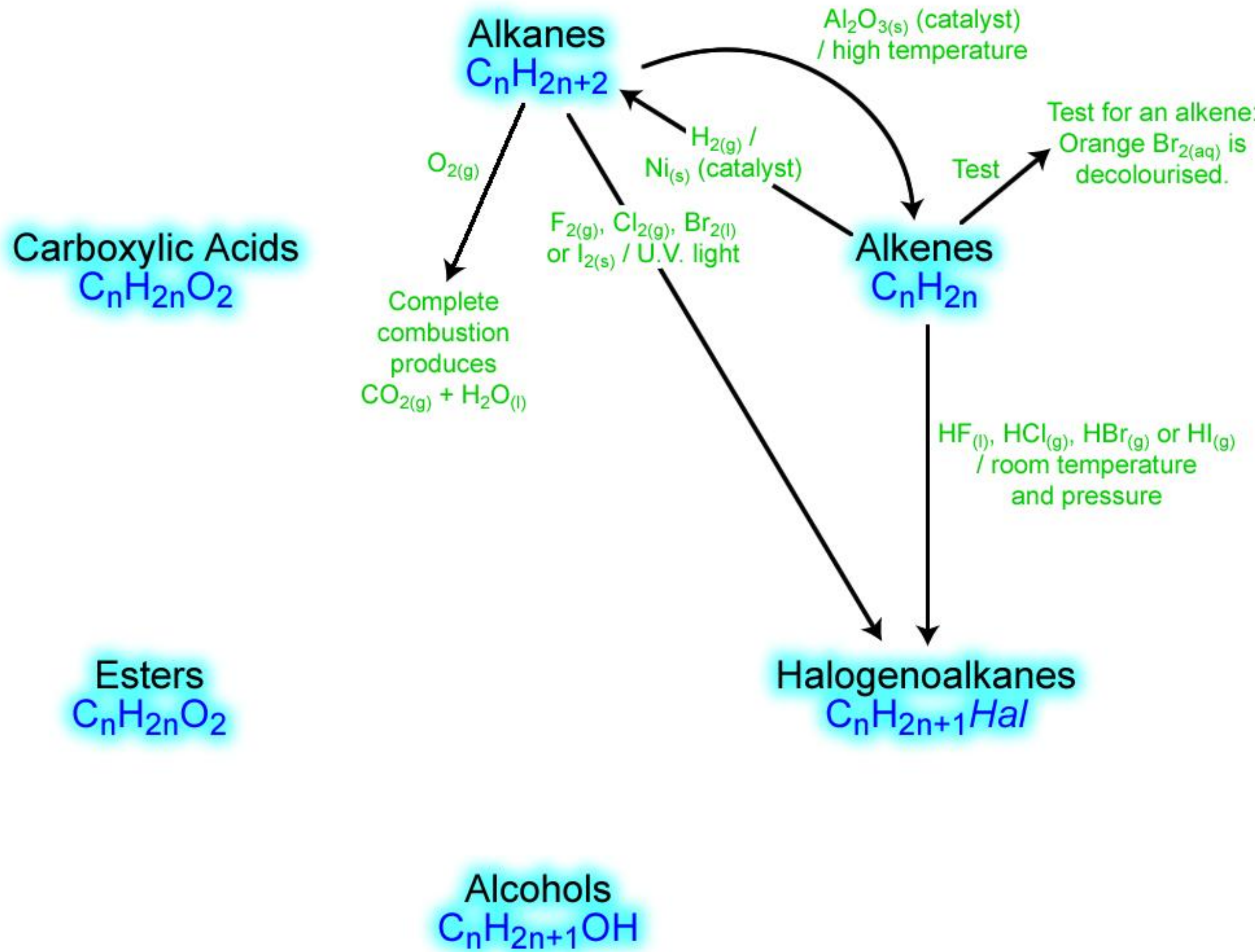
Organic Chemistry

Summary: Reactions of Organic Compounds



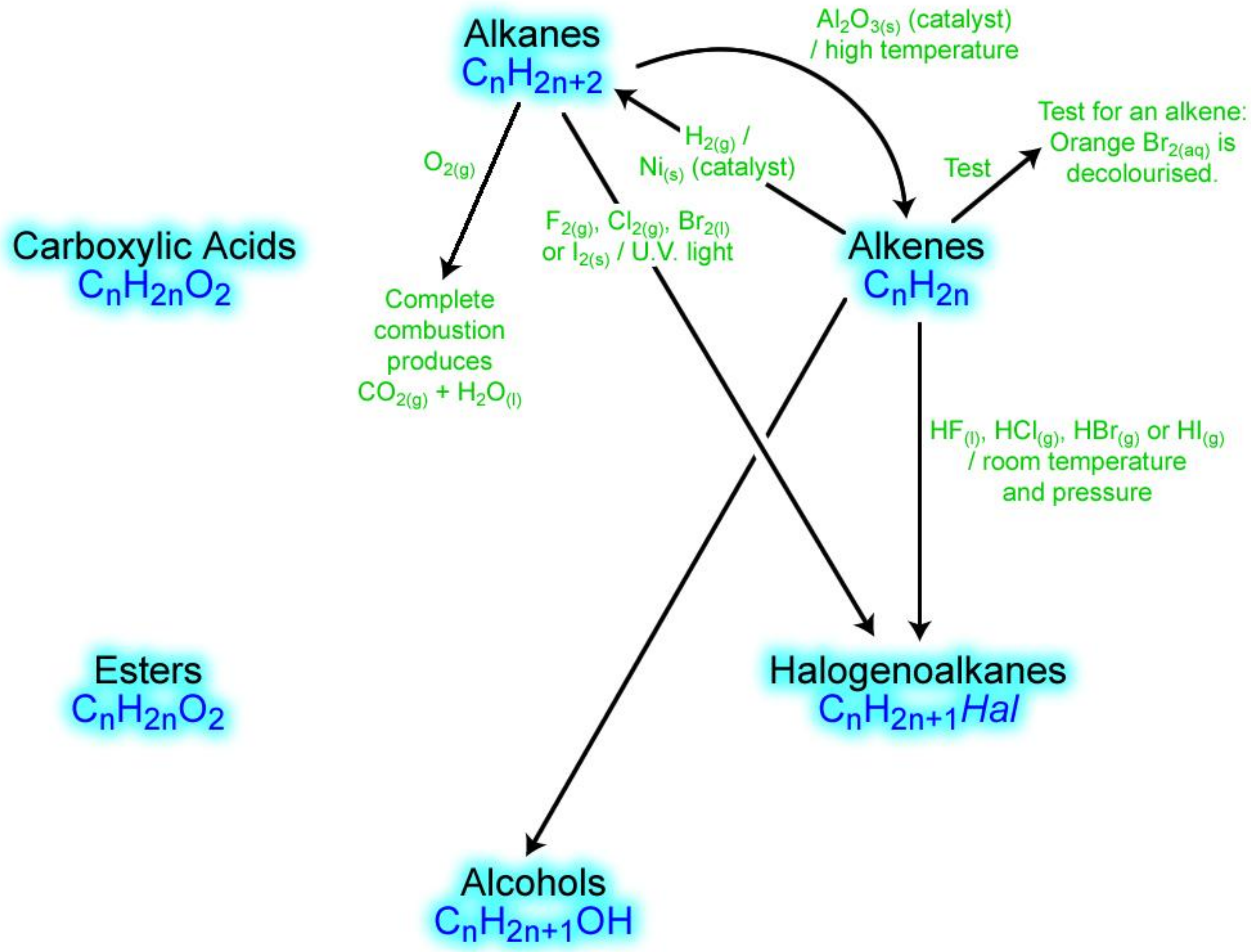
Organic Chemistry

Summary: Reactions of Organic Compounds



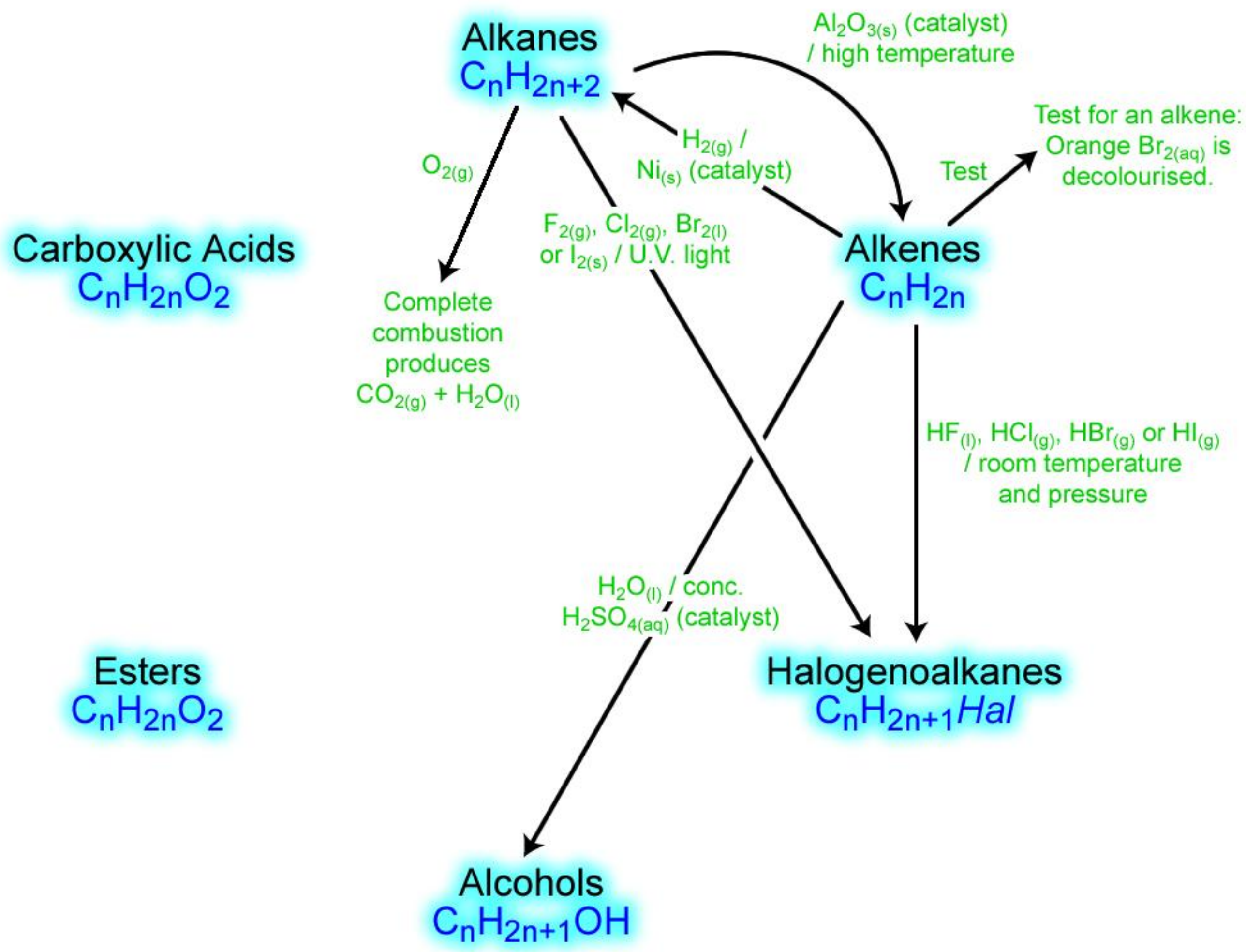
Organic Chemistry

Summary: Reactions of Organic Compounds



Organic Chemistry

Summary: Reactions of Organic Compounds



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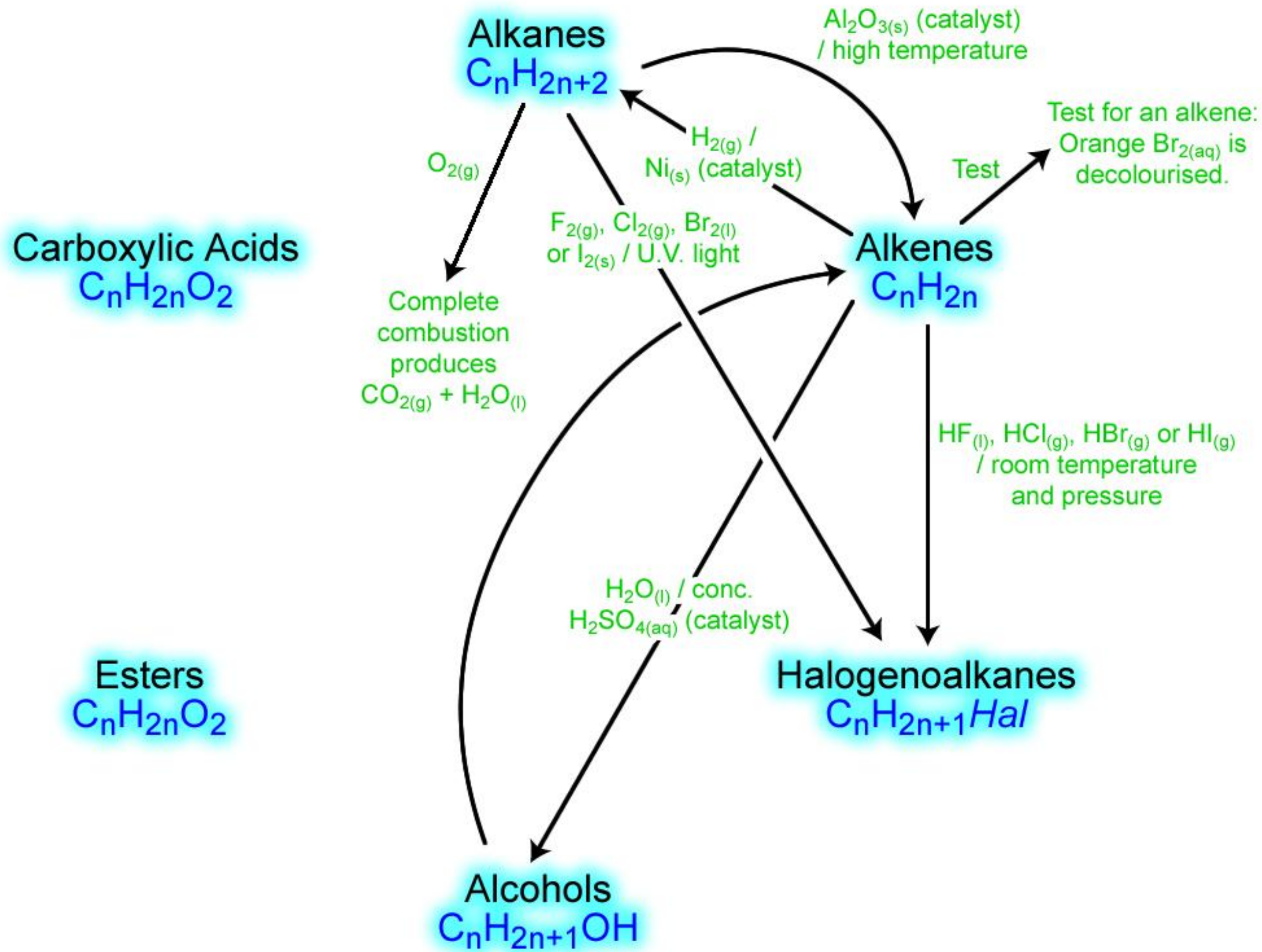

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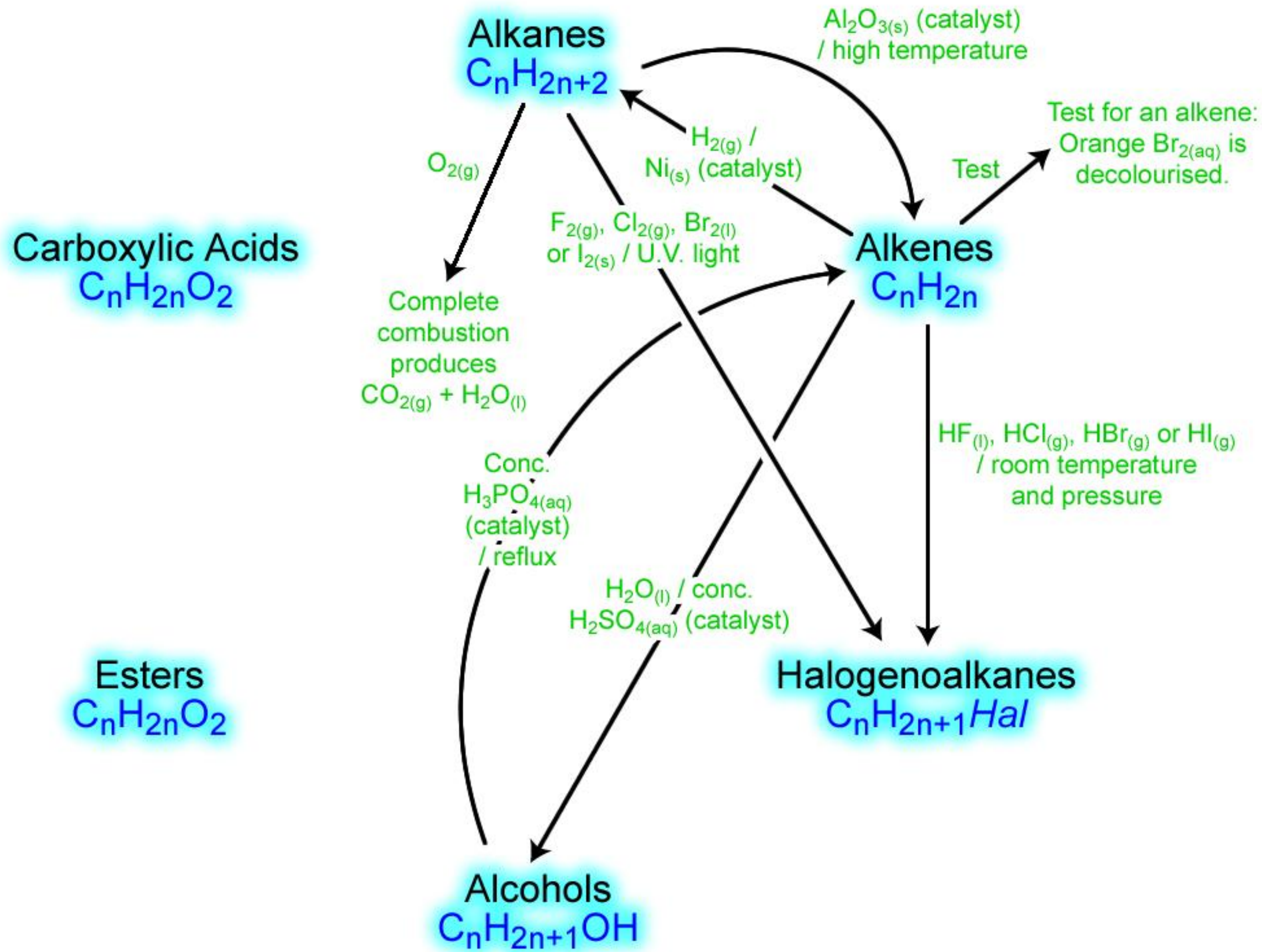

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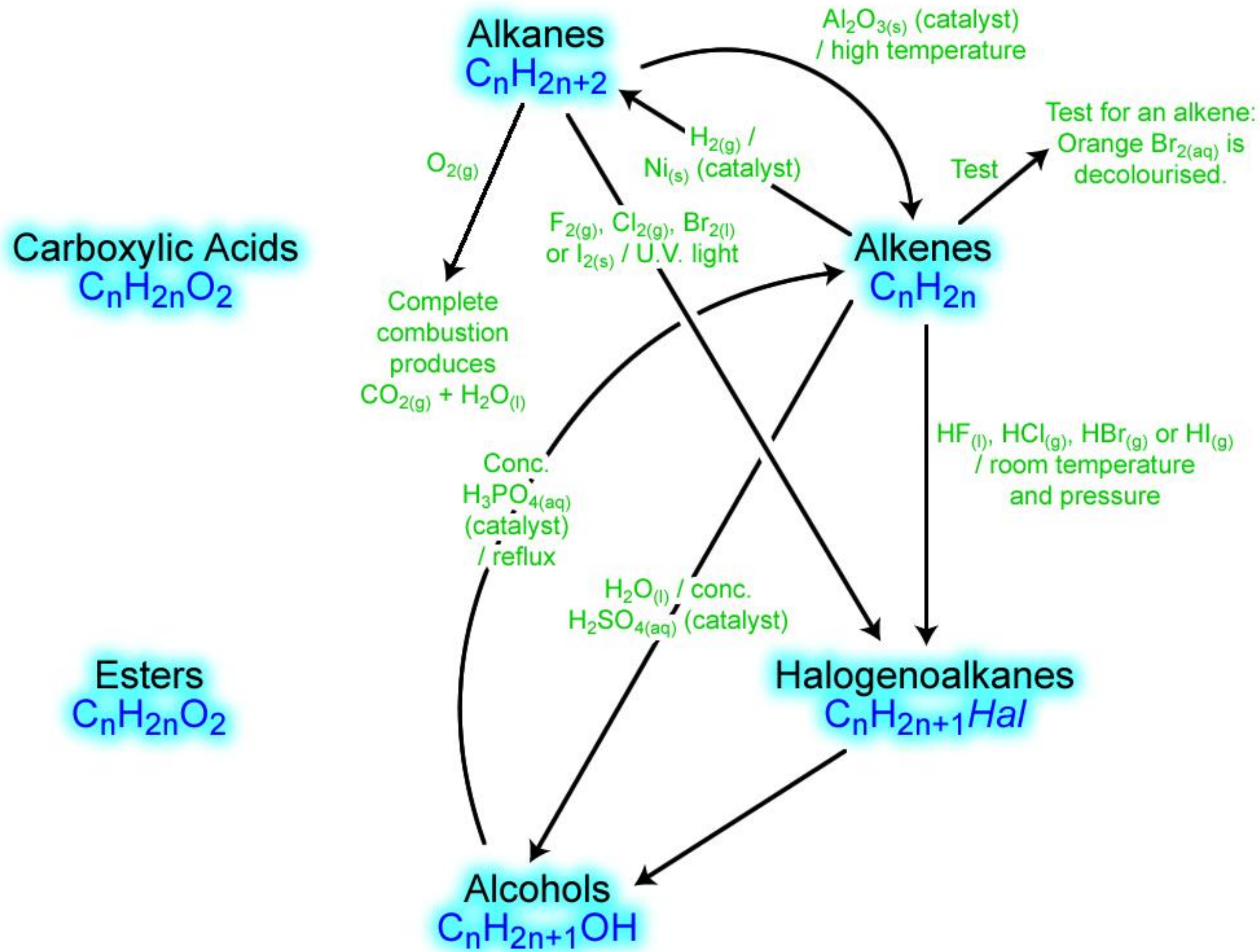

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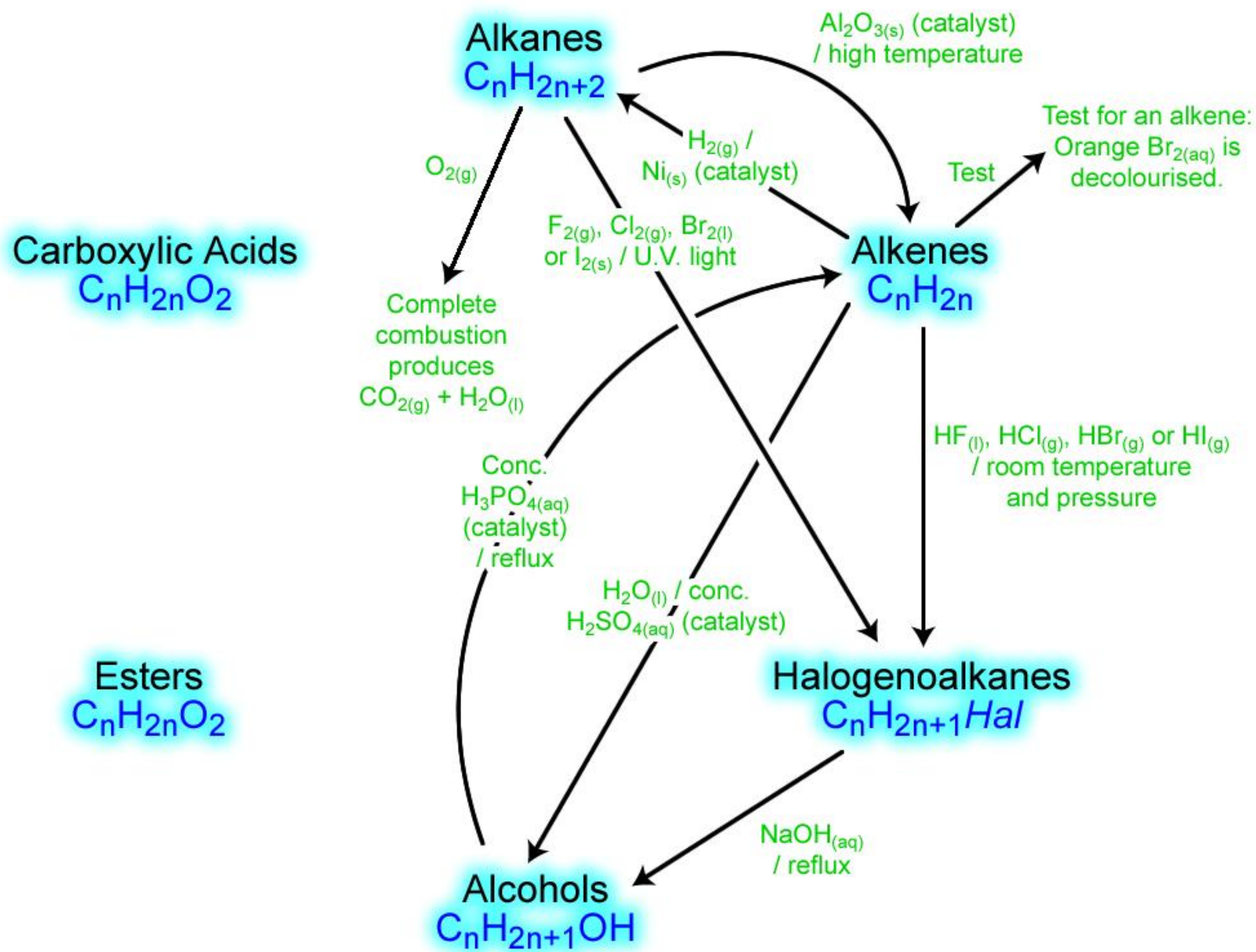

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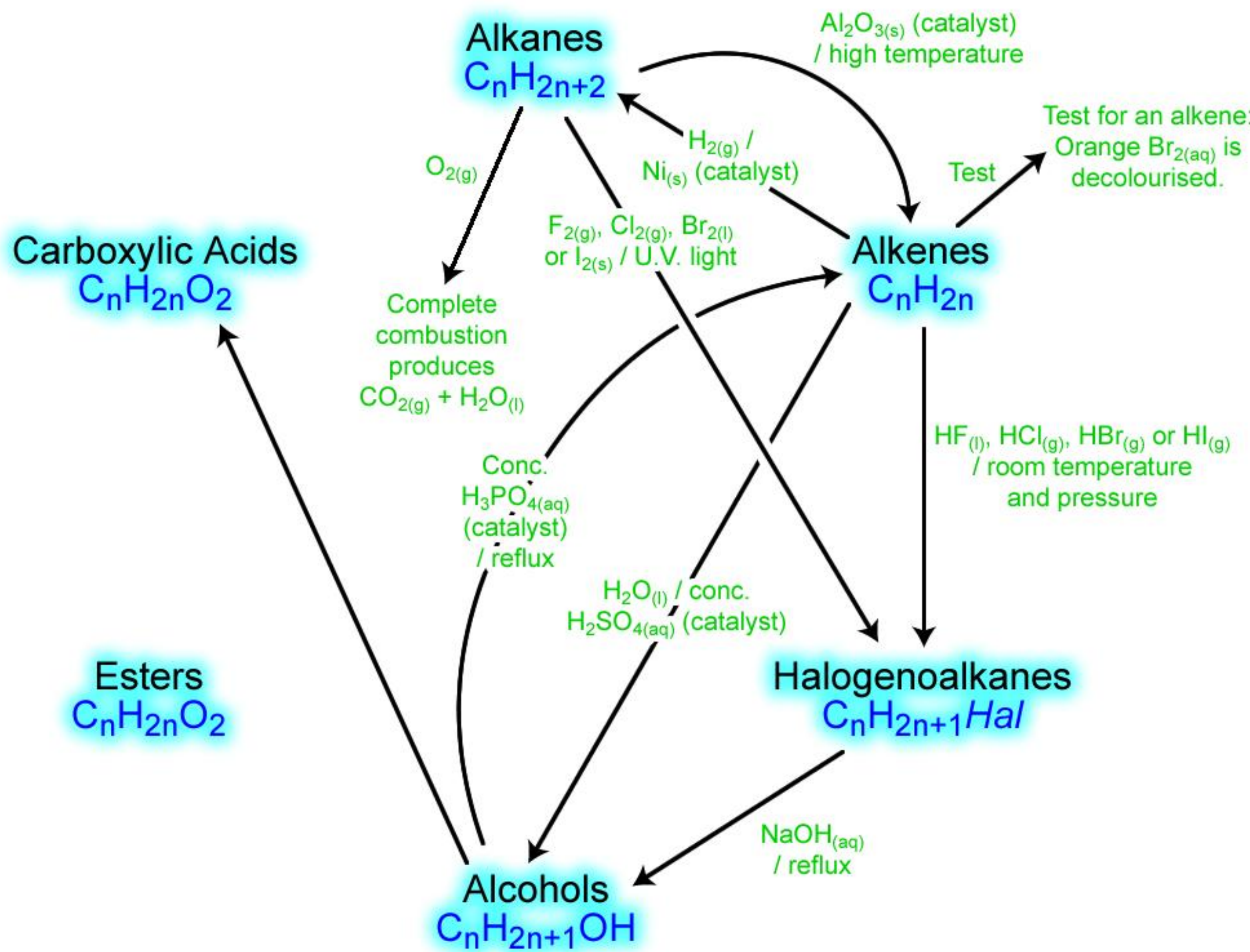

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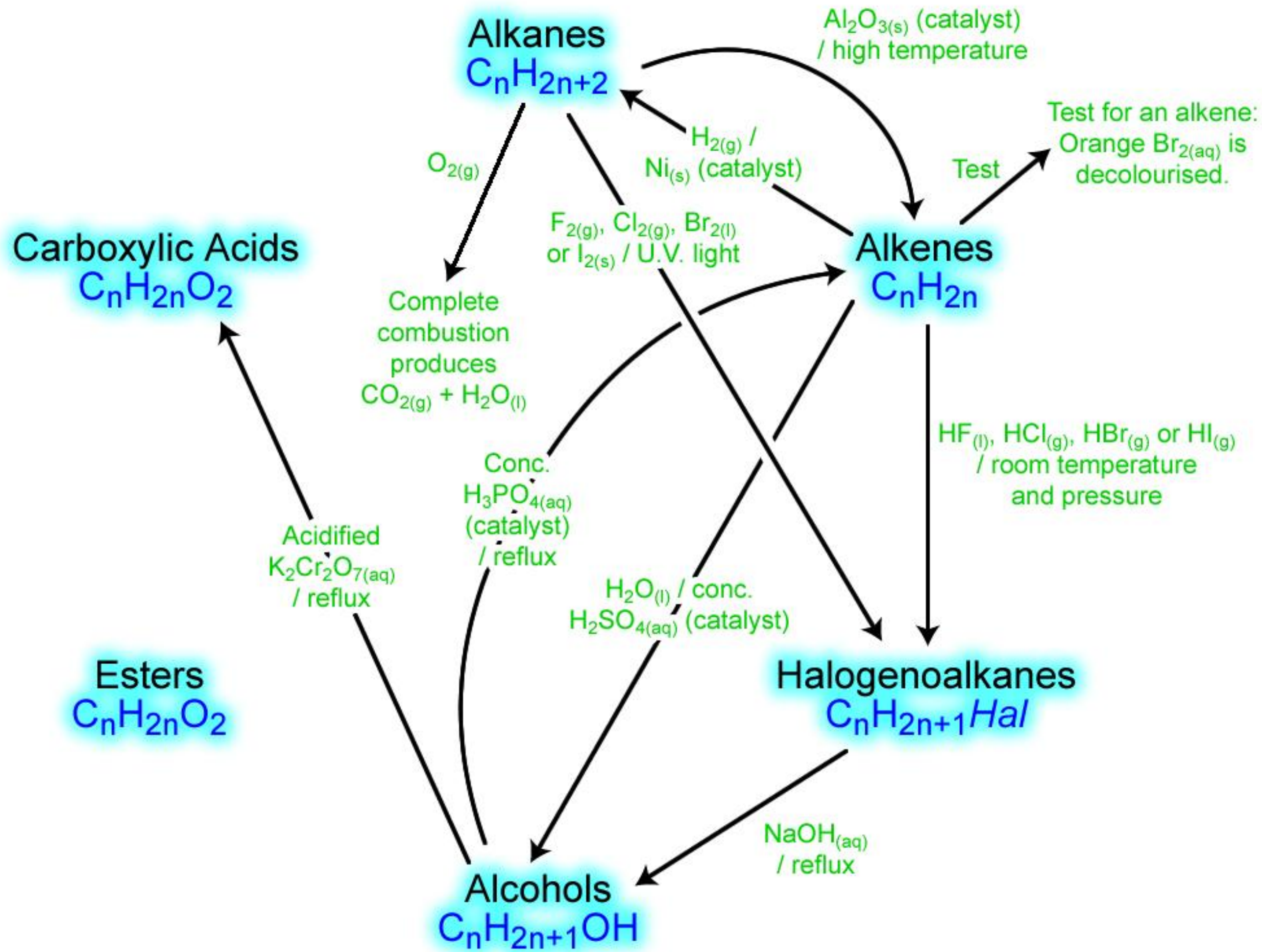

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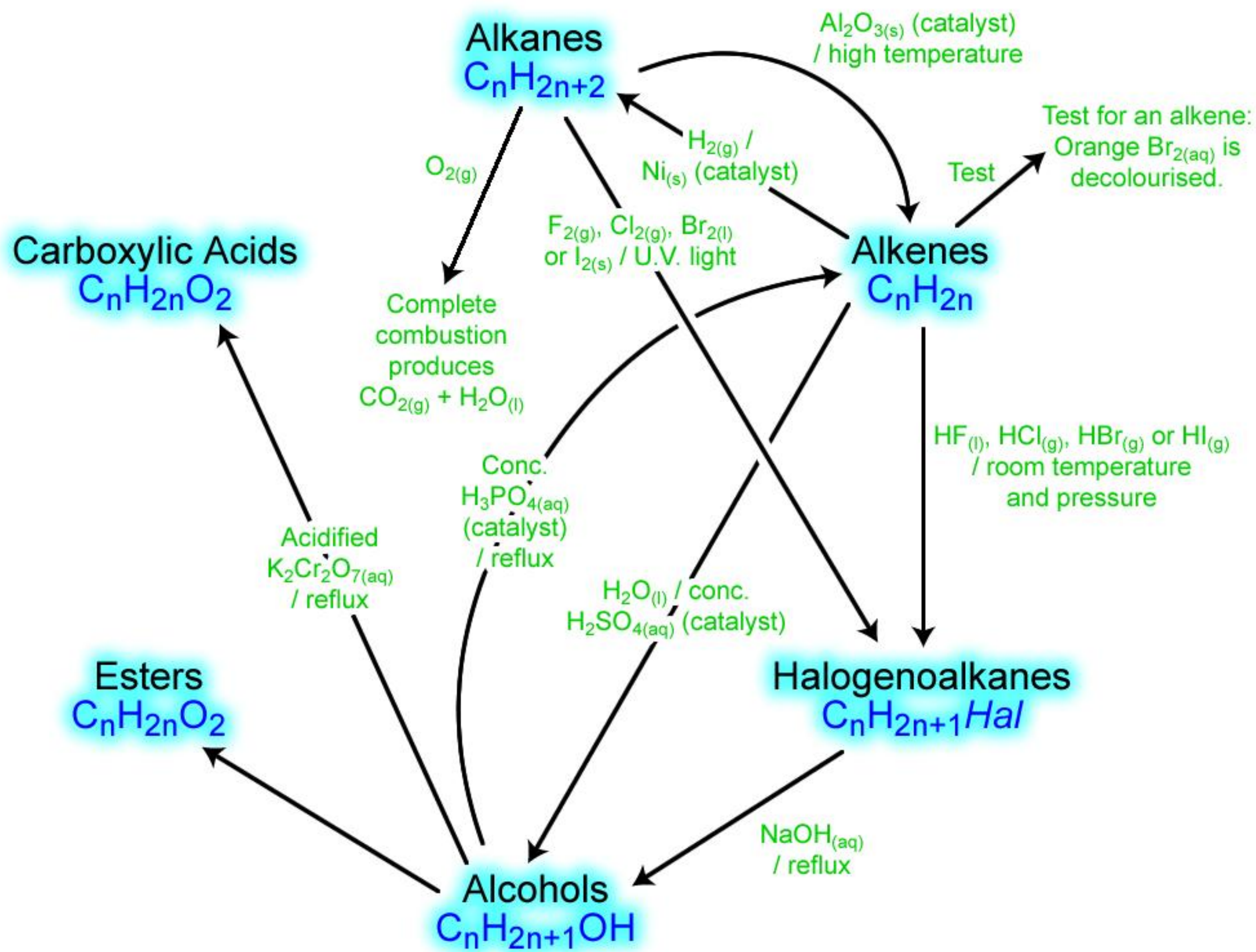

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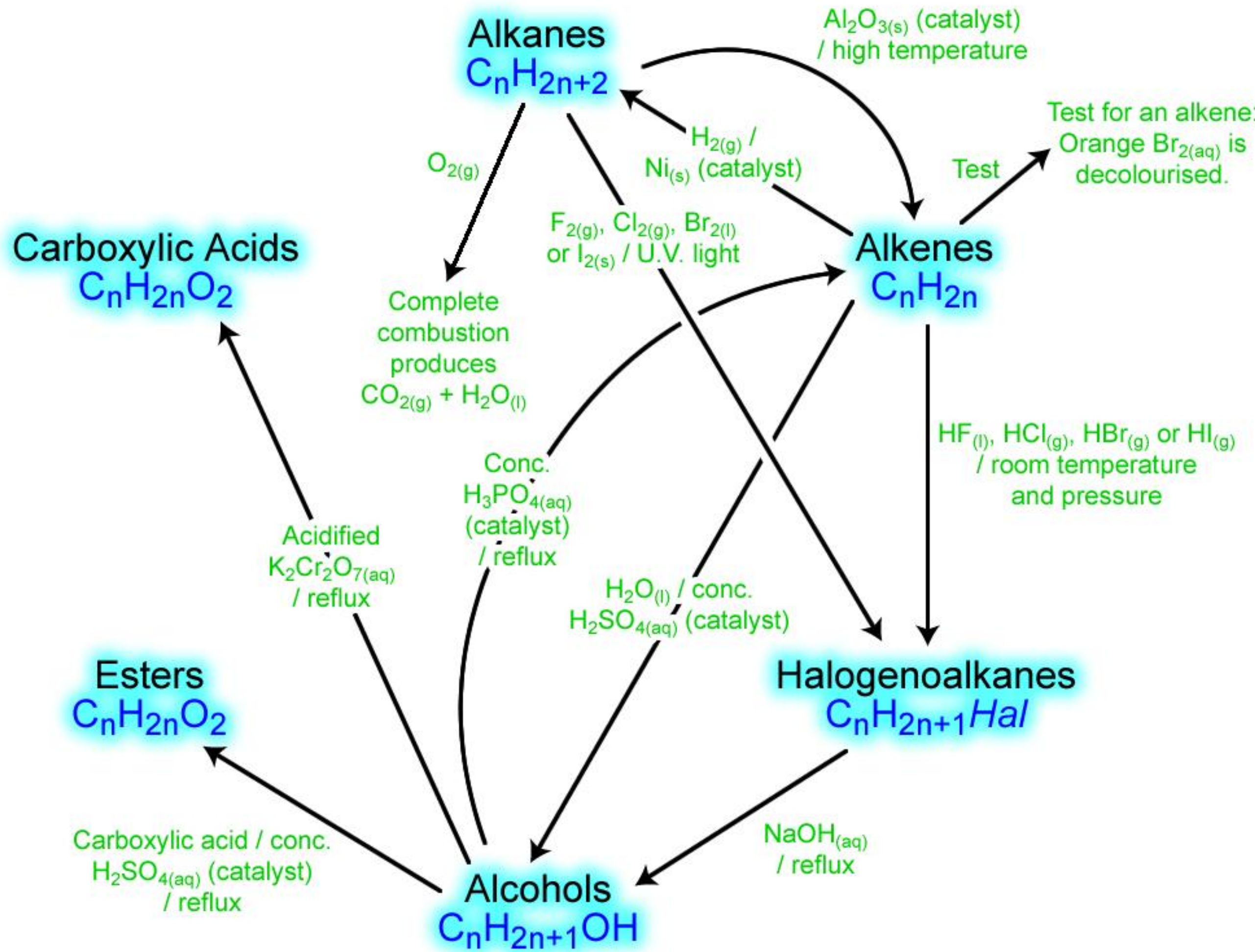

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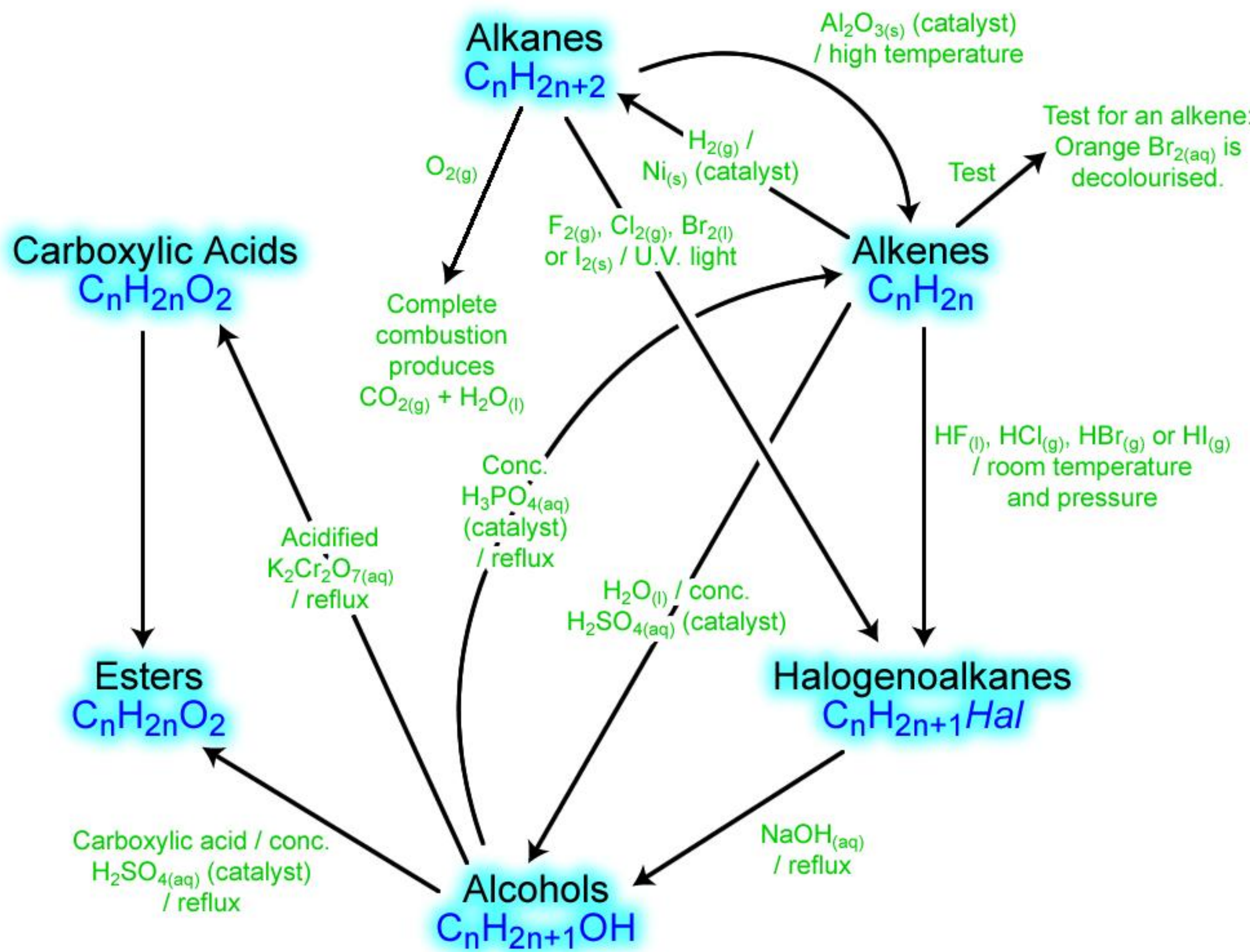

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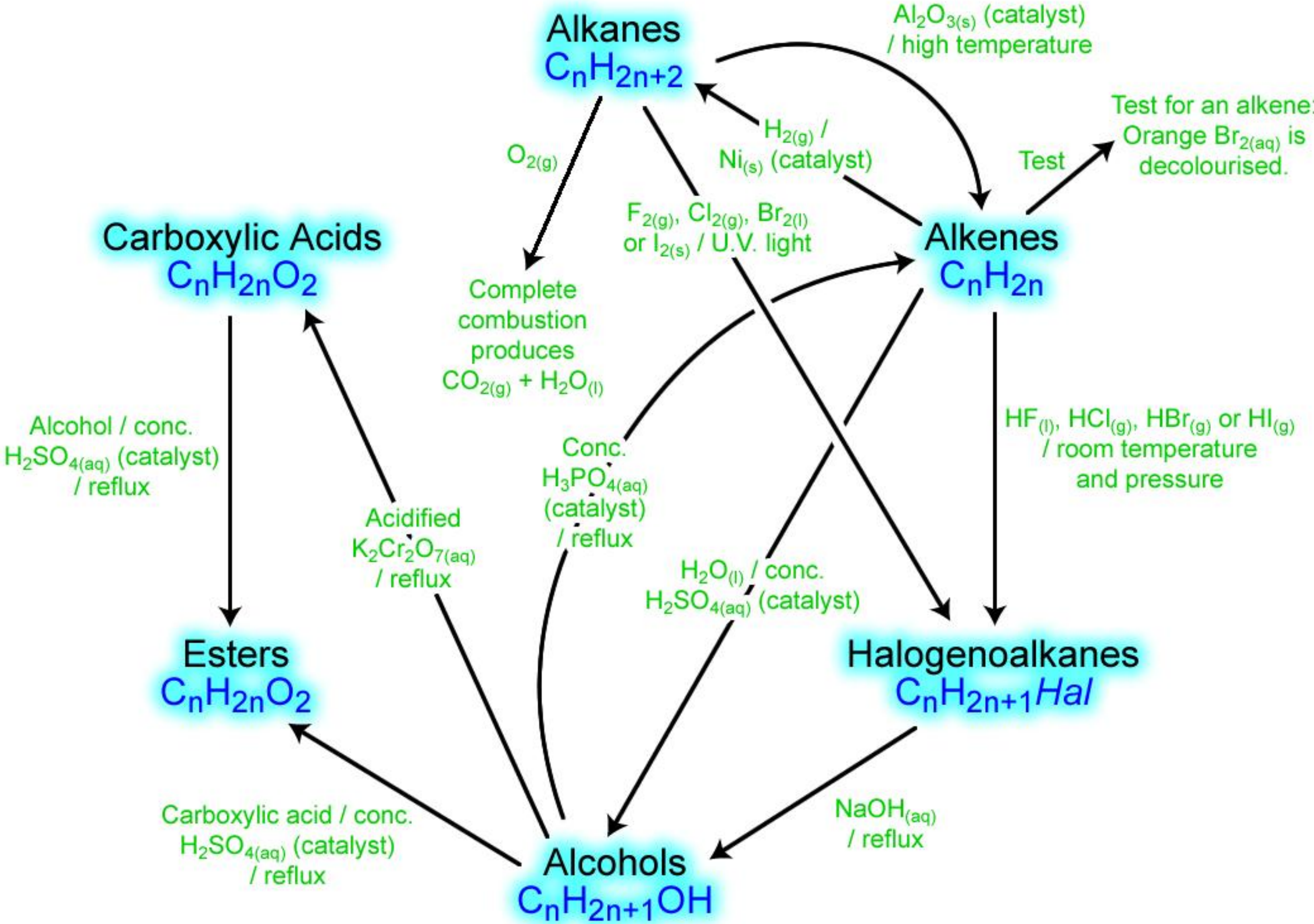

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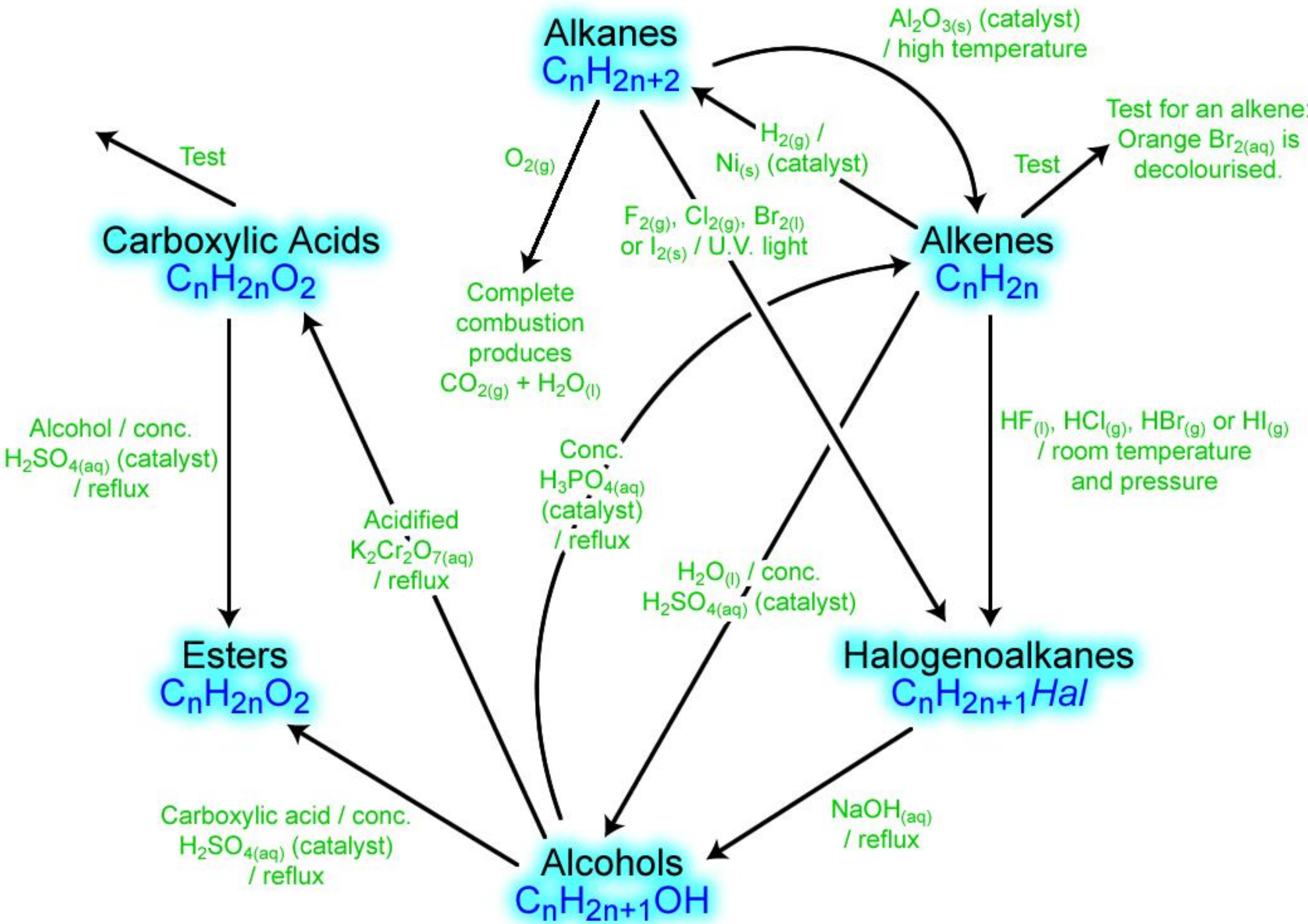

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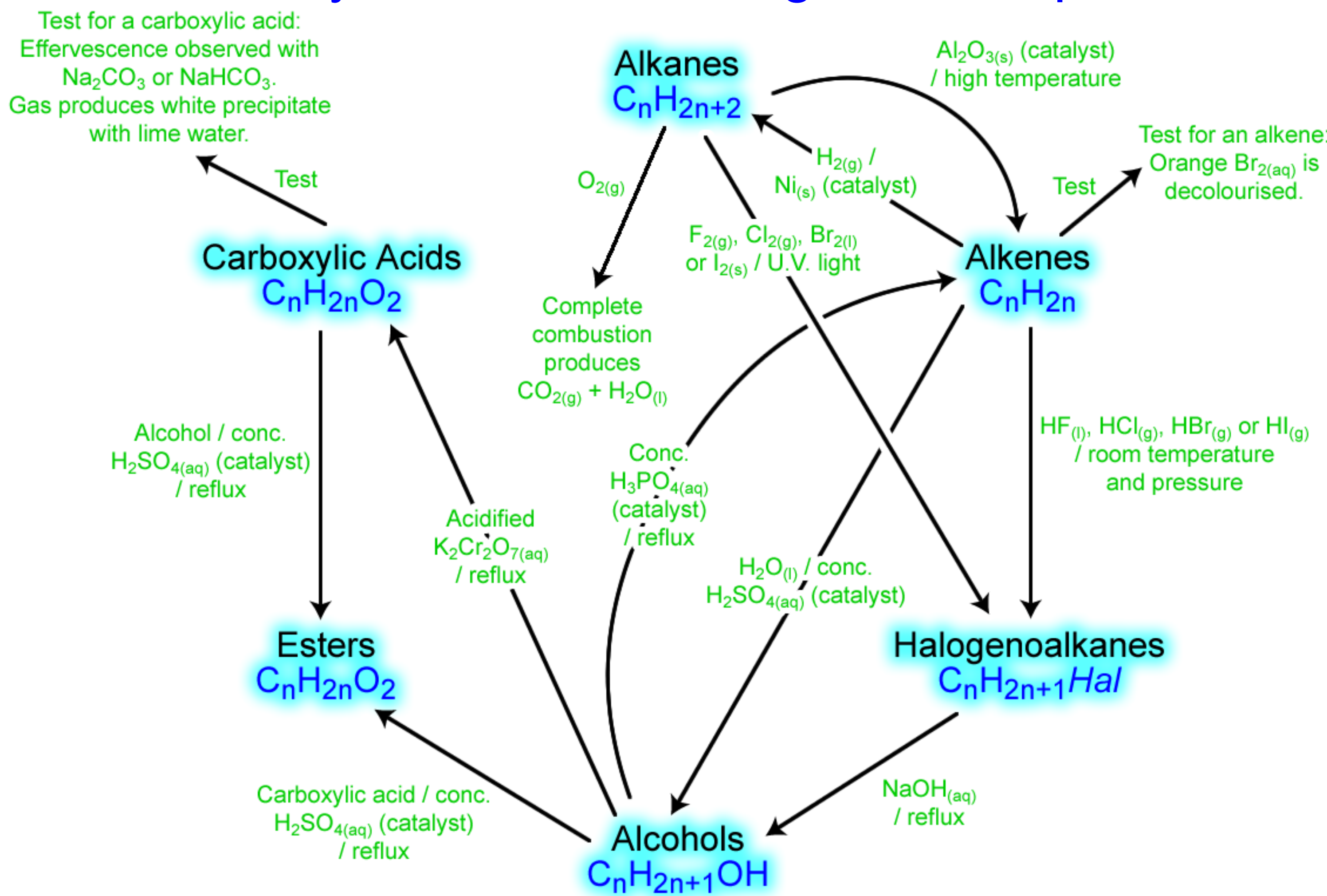

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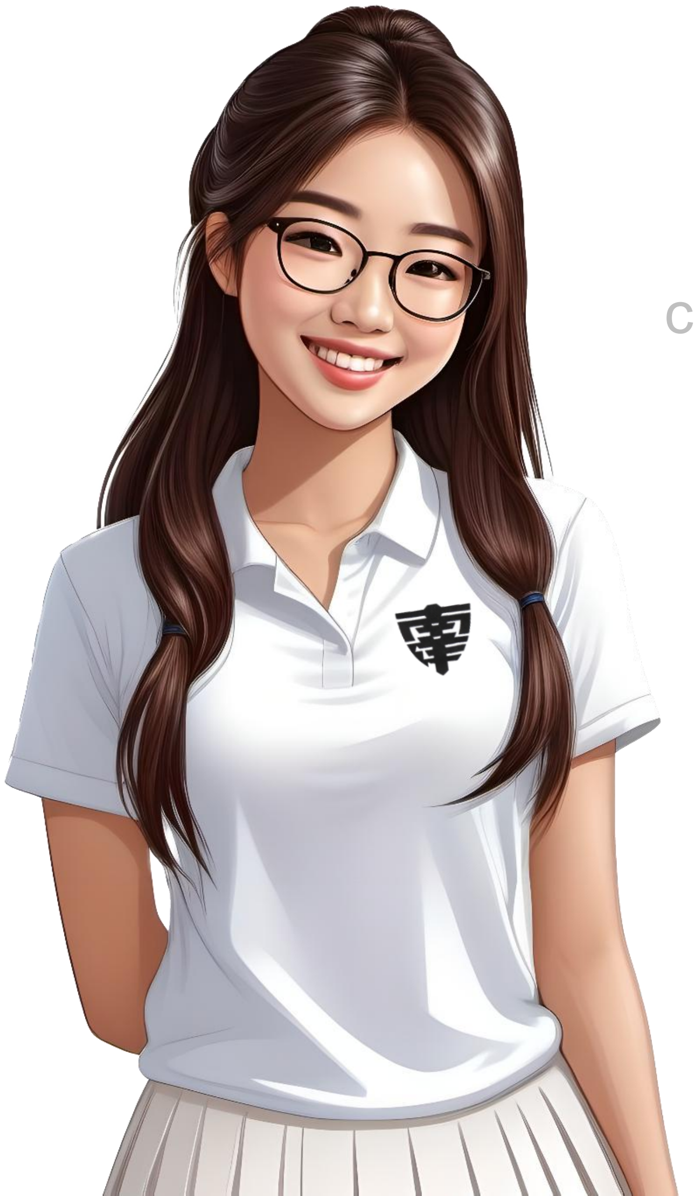

Presentation on
Organic Chemistry
by Dr. Chris Slatter

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