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## Chapter 26: Pathways in Organic Reaction

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### Chapter Overview

With more than ten million carbon compounds known to exist, and with tens of thousands of new compounds being added to the list every year, the study of carbon chemistry appears to be a daunting task. However a search for patterns in the reactions of carbon compounds reveals surprising simplicity, both in the types of reactions they undergo and in the ways in which their reactions are initiated.

Reactions involve the breaking and making of bonds. An electron pair bond (A–B) can only break in two ways: either the electron pair is shared out in **homolytic fission** ( $A-B \rightarrow A\cdot + B\cdot$ ) or it ends up on one of the previously bonded atoms in **heterolytic fission** ( $A-B \rightarrow A^+ + :B^-$ ). In the former, each of the fragments ( $A\cdot + B\cdot$ ) known as radicals, ends up with an unpaired electron. In the latter, the fragment which gets the electron pair carries a negative charge ( $:B^-$ ); the fragment which loses out ( $A^+$ ), a positive charge.

What can happen to molecules, which are built out of largely unreactive carbon carbon (C–C) and carbon hydrogen (C–H) bonds, is limited. The reactions carbon compounds undergo can be classified as **substitution**, **addition** or **elimination**. In substitution reactions, an atom or group of atoms substitutes another atom or group of atoms in a molecule; in addition reactions, an atom or group of atoms is added onto a molecule; in elimination reactions, an atom or group of atoms is eliminated from a molecule.

### After studying chapter 26 you students will be able to

- State that alkanes can react with halogens and distinguish between *homolytic* and *heterolytic fission*.
- Distinguish between *primary*, *secondary* and *tertiary halogenoalkanes*.
- Describe and explain the  $S_N1$  and  $S_N2$  mechanisms in nucleophilic substitution.
- Describe and explain the molecularity for the  $S_N1$  and  $S_N2$  mechanisms.
- Describe how the rate of nucleophilic substitution in halogenoalkanes depends on both the identity of the halogen and whether the halogenoalkane is primary, secondary or tertiary.
- Outline how the relative rate of nucleophilic substitution is affected by different nucleophiles.
- Describe and explain inductive and steric effects of substituents on substitution reaction.
- Define the terms *rate-determining step*, *molecularity* and *activated complex*.
- Describe the relationship between mechanism, order, and rate, determining step and activated complex.
- Describe and explain the reactions of 2, 4-dinitrophenylhydrazine with aldehydes and ketones.
- Describe and explain the electrophilic addition reactions of symmetrical alkenes.

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- Apply Markovnikov's rule to predict the outcome of the electrophilic addition reactions of asymmetrical alkenes.
- State and explain the relative stabilities of carbocations in order to account for Markovnikov's rule.
- Describe and explain the mechanism for the addition of hydrogen cyanide to aldehydes and ketones, followed by hydrolysis to give carboxylic acids.
- Describe and explain the mechanism for the nitration of benzene.
- Describe and explain the chlorination and alkylation reactions of benzene and methylbenzene in the presence of a halogen carrier.
- Describe and explain the directing effects and relative rates of reaction of different substituents on a benzene ring.
- Describe and explain the relative rates of hydrolysis of halogenated benzene compounds.
- Describe the dehydration reaction of alcohols to form alkenes.
- Describe the mechanism involved in the manufacture of low-density polyethene.
- Describe the mechanism for the elimination of water from alcohols.
- Describe and explain the mechanism for the elimination of HBr from bromoalkanes.
- Describe and explain the reactions of 2,4-dinitrophenylhydrazine with aldehydes and ketones.

### **Students will achieve these objectives by acquiring the following knowledge and understanding**

- Ions are formed when covalent bonds break heterolytically; free radicals are formed when covalent bonds break homolytically.
- Free radicals have a range of stabilities; the least stable only exist as fleeting intermediates in reactions.
- Alkanes undergo free radical substitution when they react with halogens in the presence of sunlight. Radical reactions can take place very rapidly. This is because once initiated further 'shots' of activation energy are not needed to propagate the reaction.
- Nucleophiles are molecules or ions which react by donating an electron pair to an electron deficient carbon.
- Nucleophilic substitution occurs when the nucleophile replaces an atom or group of atoms in a molecule.
- Reaction conditions can affect the pathway a reaction takes. In aqueous solution hydroxide ions substitute the halogen in halogenoalkanes; in ethanol an elimination reaction produces an alkene.
- Nucleophilic addition occurs when a nucleophile adds onto to a carbonyl group. The nucleophile pushes an electron pair out of the double bond as it bonds with the electron deficient carbon.

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- Electrophilic addition occurs when an electrophile bonds by pulling electrons out of a double (or triple) bond. A carbo cation is formed as an intermediate in this type of reaction.
- Radical addition (e.g. in polymerization) takes place when a free radical attacks a double bond to make a new C–C bond at the same time as generating a new radical to propagate the reaction.
- Electrophilic substitution occurs when an electrophile bonds by pulling a pair of  $\pi$  electrons out of the delocalised system in benzene rings. The delocalised system then re-establishes itself by using the electron pair from the heterolytic fission of a carbon hydrogen bond.

### Lesson 26.1 – Types of Reactions

Topics – Nucleophilic substitution, reactive sites, homo and heterolytic fission, attacking non-polar bonds, types of reactions – Demonstrate with models

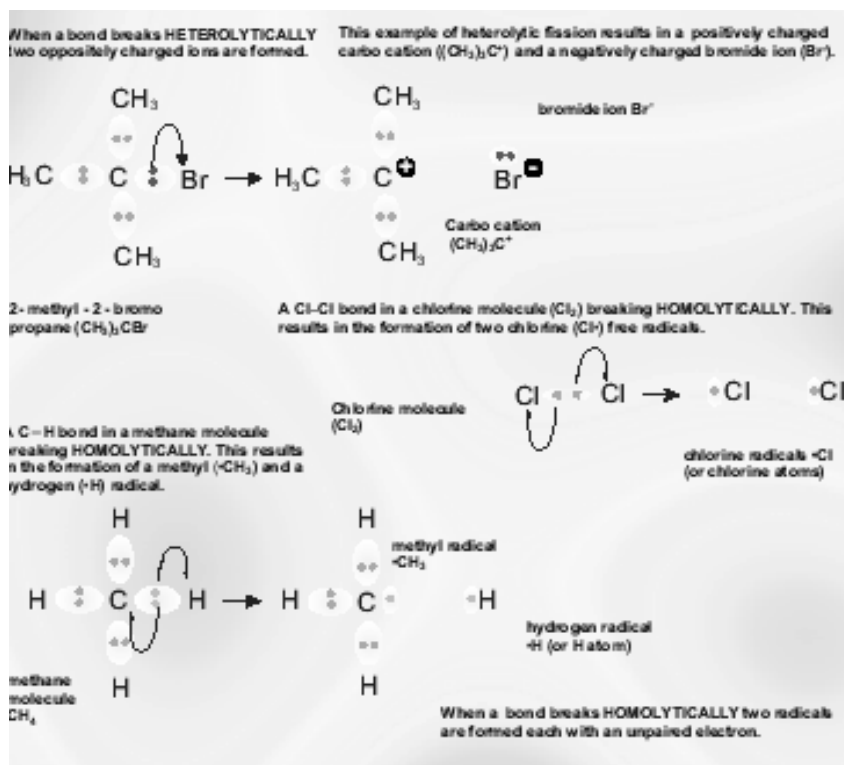
Relate subject matter to chapter 20

Homework – assign chapter 26 study question 1

Present class notes 26.1a to 26.1e

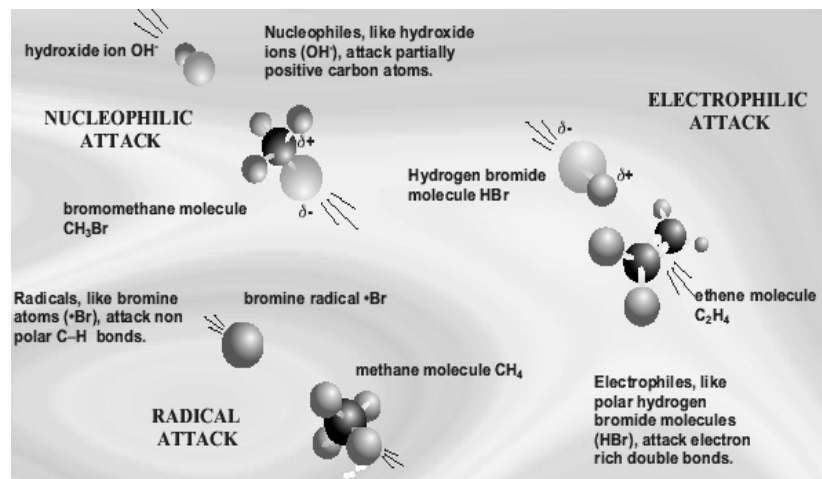
#### 10 minutes **introduction**

Ask students to suggest a strategy for studying the millions of carbon compounds that exist and the thousands that are being discovered every year. Lead to question: classify according to structure or reaction? Lead discussion to what happens in a reaction; making and breaking bonds: **homolytic** and **heterolytic** fission and the types of reaction that can take place; **substitution**, **addition** and **elimination**.



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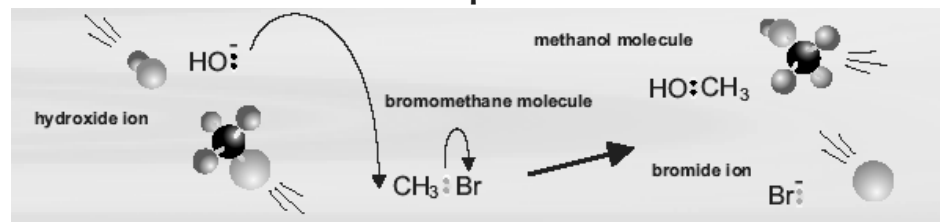
25 minutes **development** reactive sites in carbon compounds



Review: Polar O-H bonds are reactive e.g. in carbon compounds like ethanoic acid ( $\text{CH}_3\text{COOH}$ ) and phenol ( $\text{C}_6\text{H}_5\text{OH}$ ), non polar C-H bonds are unreactive. Ask question: if polar water molecules can attack polar bonds is it likely that other charged or partially charged particles could do the same? Lead to definition of **nucleophiles** that are

attracted to positively charged ends of polar bonds and **electrophiles** to negatively charged or electron rich sites. Although C-H bonds are stable they can be made to react. How? .. by breaking the bond homolytically with a **free radical**.

20 minute **consolidation** nucleophilic attack



Take another look at hydroxide ions ( $\text{O-H}^-$ ) attacking polar O-H bonds in molecules like phenol ( $\text{C}_6\text{H}_5\text{OH}$ ). Pose

question what would happen if hydroxide ions attacked a carbon halogen bond (C-Hal)? What experiment could you carry out to propose a mechanism for the reaction (determine the order of the reaction)?

5 minutes **summary**

- Ions are formed when covalent bonds break heterolytically; free radicals are formed when covalent bonds break homolytically.
- Nucleophiles are molecules or ions which react by donating an electron pair to an electron deficient carbon.
- Nucleophilic substitution occurs when the nucleophile replaces an atom or group of atoms in a molecule.

### Lesson 26.2 – Nucleophilic Substitution

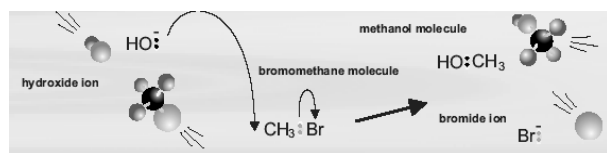
Review chapter 26 study question 1

Homework – assign chapter 26 study question 2

Present class notes 26.2a to 26.2c

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### 15 minutes **introduction**



Ask students to use experimental evidence that the reaction is 2<sup>nd</sup> order (rate =  $k [\text{CH}_3\text{Br}] [\text{OH}^-]$ ) to propose a mechanism for what happens. Lead discussion to the involvement of both reactants in rate determining step and

a mechanism with the hydroxide ions attacking the carbon atom from the opposite side to the bulky bromine atom. Use models to illustrate. Describe reaction as S<sub>N</sub>2 Substitution Nucleophilic Bimolecular (bimolecular because both of the reactants appear in the rate equation).

### 35 minutes **development**

Effect of methyl groups (CH <sub>3</sub> ) on the relative rates of nucleophilic substitution.	
bromoalkane	relative rate
CH <sub>3</sub> Br	100
CH <sub>3</sub> CH <sub>2</sub> Br	8
(CH <sub>3</sub> ) <sub>2</sub> CHBr	1

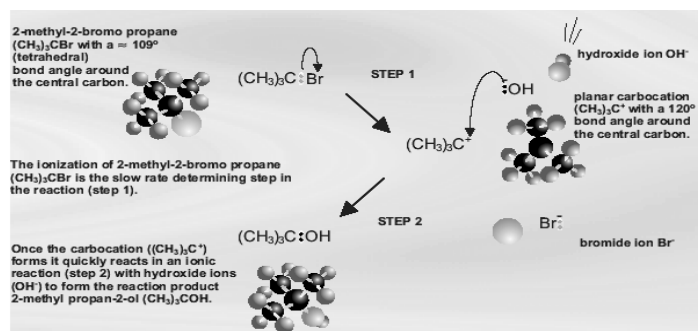
the greater the number of methyl (CH<sub>3</sub>) groups on the carbon where substitution takes place, the slower the rate of reaction.

Present students with experimental data from similar investigations carried out with bromoethane (CH<sub>3</sub>CH<sub>2</sub>Br) and 2-bromopropane (CH<sub>3</sub>)<sub>2</sub>CHBr. Use models to show how bulky methyl groups (CH<sub>3</sub>) could affect the relative rates of substitution. Ask students to then predict the relative rate of reaction of 2-bromo-2-methyl propane (CH<sub>3</sub>)<sub>3</sub>CBr. Surprisingly, this reaction goes much faster and is 1<sup>st</sup> rather than 2<sup>nd</sup> order, rate =  $k [(\text{CH}_3)_3\text{CBr}]$ . Lead discussion to a different mechanism for this reaction consistent with rate equation: a rate determining 1<sup>st</sup> step

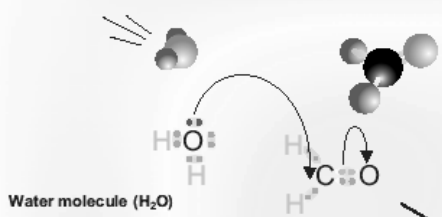
radical	cation	enthalpy of formation
CH <sub>3</sub>	CH <sub>3</sub> <sup>+</sup>	55 kJ
CH <sub>3</sub> CH <sub>2</sub>	CH <sub>3</sub> CH <sub>2</sub> <sup>+</sup>	48kJ
(CH <sub>3</sub> ) <sub>2</sub> CH	(CH <sub>3</sub> ) <sub>2</sub> CH <sup>+</sup>	43kJ
(CH <sub>3</sub> ) <sub>3</sub> C	(CH <sub>3</sub> ) <sub>3</sub> C <sup>+</sup>	41kJ

producing a **carbocation** (CH<sub>3</sub>)<sub>3</sub>C<sup>+</sup> followed by a rapid 2<sup>nd</sup> step. Describe as an S<sub>N</sub>1 reaction: Substitution Nucleophilic unimolecular (unimolecular

because only one reactant appears in the rate equation). Discuss the factors that affect the stability of carbo cations (electron releasing methyl groups stabilize the ions by delocalizing the charge). Discuss how the solvent can affect the rate at which a nucleophilic reaction can occur.



### 10 minutes **consolidation** and **summary**



Ask students to consider other reactive sites which could be attacked by nucleophiles (e.g. carbonyl group C=O). In this case, with a double bond attaching the carbon to an oxygen, would the mechanism be the same? Could something else happen? **TOK:** Agreement between rate equation and a suggested mechanism only provides evidence to support a

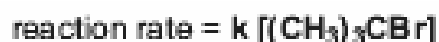
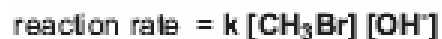
reaction mechanism. Disagreement disproves the mechanism.

### Lesson 26.3 – Nucleophilic Addition

Homework – assign chapter 26 study questions 3 and 4  
Present class notes 26.3a to 26.3d

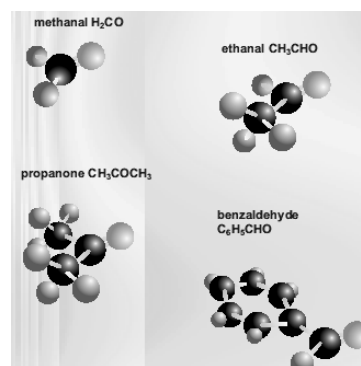
#### 10 minutes **introduction**

Summarize what makes a reactive site susceptible to nucleophilic attack. Ask students to explain how the postulated mechanisms for nucleophilic substitution reactions are consistent with experimental evidence (rate laws).

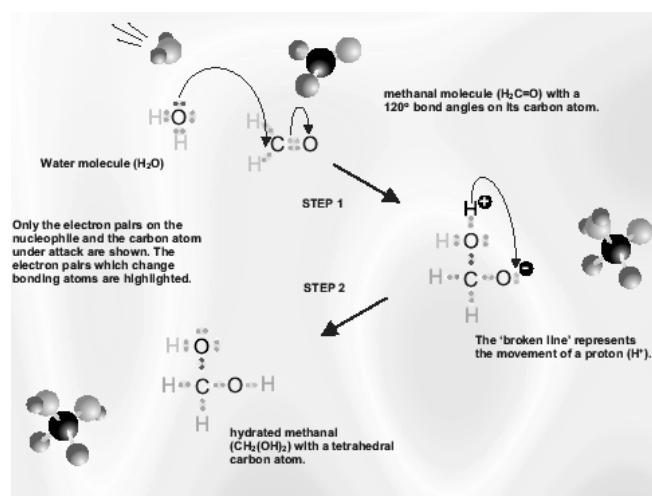


#### 25 minutes **development**

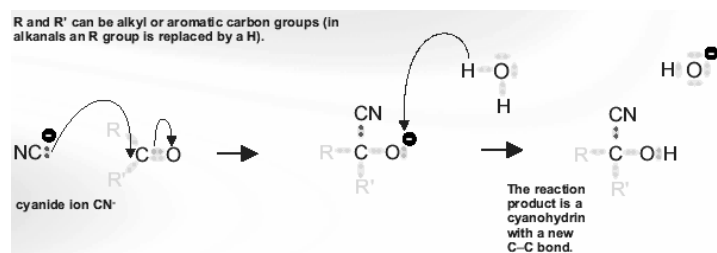
Describe the shape (planar,  $120^\circ$  bond angle) and the electron distribution (electron rich with  $\pi$  electrons drawn towards electronegative oxygen) in the carbonyl group ( $\text{C}=\text{O}$ ). Lead students to the conclusion that if attacked by a nucleophile, with a pair of electrons keen to make a new bond, the double bond must open up. In this case



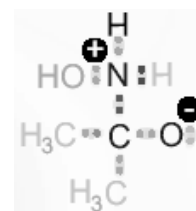
there will be an addition rather than a substitution reaction. Discuss how the relative rates of addition to alkanals and alkanones provides evidence for the supposed reaction intermediate. Lead students to a consideration of how **steric** and **inductive effects** can **influence** the stability of the intermediate and hence the **rate** at which the reaction takes place.



#### 20 minutes **consolidation**



Outline the addition of  $\text{CN}^-$  to a carbonyl group.



Ask students what is significant in the reaction (a new C-C bond is made). The use of Grignard Reagents to introduce carbon chains and rings into molecules could also be

mentioned. Ask students to draw the intermediate formed when a nucleophile with an amine group (e.g.  $\text{NH}_2\text{OH}$ ) attacks the carbonyl group ( $\text{C}=\text{O}$ ) in propanone ( $\text{CH}_3\text{COCH}_3$ ).

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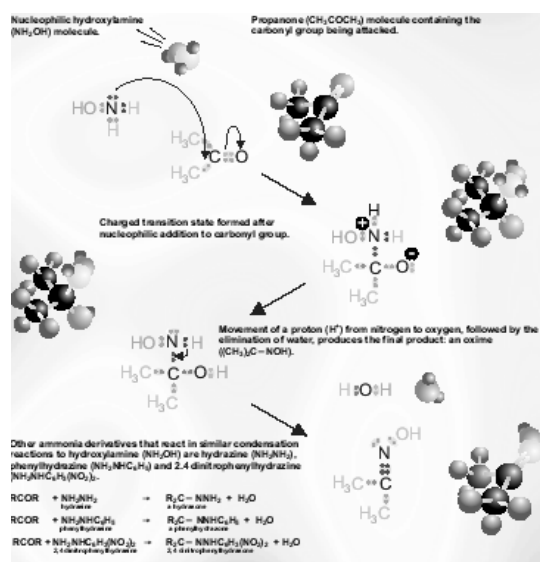
### 5 minutes **summary**

- Nucleophilic addition occurs when a nucleophile adds onto to a carbonyl group. The nucleophile pushes an electron pair out of the double bond as it bonds with the electron deficient carbon.

### Lesson 26.4 – Electrophilic Substitution

Homework – assign chapter 26 study questions 5 and 6  
Present class notes 26.4a and 26.4b

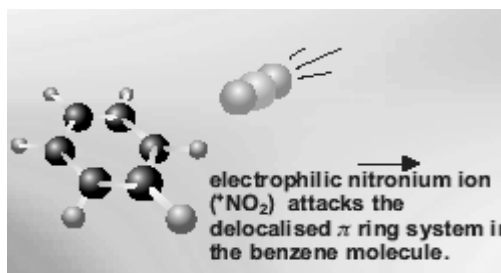
### 10 minutes **introduction**



Use the addition of hydroxylamine ( $\text{NH}_2\text{OH}$ ) to the carbonyl group ( $\text{C}=\text{O}$ ) in propanone ( $\text{CH}_3\text{COCH}_3$ ) to summarize **nucleophilic addition**. Note that the removal of a water molecule from the reaction intermediate to form a double bond is an example of an **elimination reaction**. Mention that since the product has a melting point characteristic of the original alkanal or alkanone reacted it allows this reactant to be identified. Use the opportunity to mention that melting points as well as being used to identify compounds also indicate purity (a pure substance melts suddenly; one with impurities over a range of temperatures)

### 25 minutes **development**

Attacking nucleophiles make substitution and addition reactions take place. Could similar reactions occur with electrophiles? What feature would make a reactive site susceptible to electrophilic attack? Lead discussion to electron rich double bonds and benzene rings. Ask students to predict what might happen if a powerful electrophile attacked the delocalized electrons in a benzene ring? Could it pull an electron pair out of the ring to make a new bond? If it did so it would change a particularly stable structure into a unstable one. Is it likely this unstable state could exist for long? How could it revert back to a stable ring? Lead the discussion answering these questions to a possible mechanism for electrophilic attack on a benzene ring.

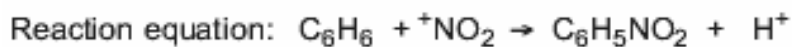


**TOK:** Agreement between rate equation and a suggested mechanism only provides evidence to support a reaction mechanism. Disagreement disproves the mechanism.

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### 10 minutes consolidation

Ask students what experiment must be carried out before a mechanism can be postulated. Lead discussion to establishing the rate equation. What is this powerful electrophile, the nitronium ion ( $\text{NO}_2^+$ ), and where does it come from?



### 5 minutes summary

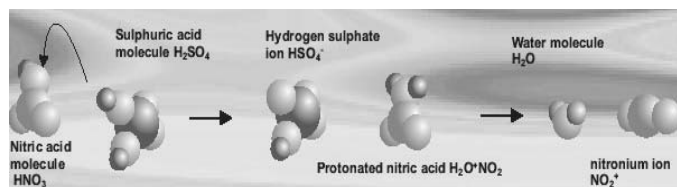
- Electrophilic substitution occurs when an electrophile bonds by pulling a pair of  $\pi$  electrons out of the delocalized system in benzene rings. The delocalized system then re-establishes itself by using the electron pair from the heterolytic fission of a carbon hydrogen bond.

### Lesson 26.5 – Electrophilic Substitution: Picking a Place on the Ring

Review chapter 26 study questions 5 and 6

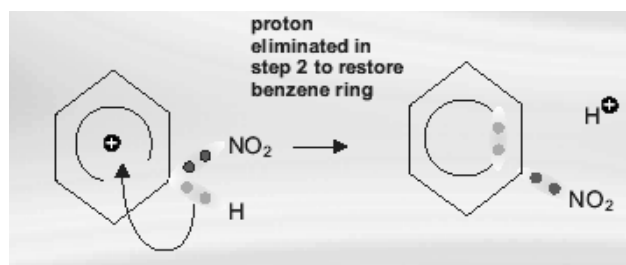
Present class notes 26.5a to 26.5c

### 10 minutes introduction



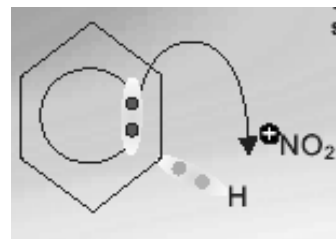
Summarize; a **powerful electrophile** is needed to attack and pull electrons out of the stable electron ring in benzene. The nitronium ion ( $\text{NO}_2^+$ ), produced when concentrated sulphuric and nitric acids are mixed, is such a reactant.

### 25 minutes development



Ask students to postulate a mechanism for the reaction consistent with the experimentally verified rate equation. Lead discussion to **possible one step** and **two step** pathways. The former would involve simultaneously breaking a C–H bond and forming a new C– $\text{NO}_2$  bond. The latter

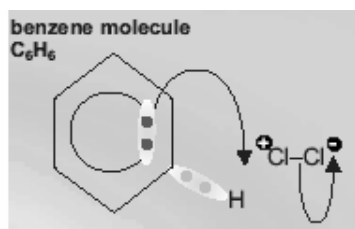
would involve the formation of a transition state, in a slow rate determining step. How to choose? Comparing the reaction rates of benzene molecules made with ordinary hydrogen with benzene made with deuterium provides the evidence. Since C–D bonds are stronger than C–H bonds, reactions in which C–H and C–D bonds are broken will take place at different rates. Since  $\text{C}_6\text{H}_6$  and  $\text{C}_6\text{D}_6$  undergo nitration at the same rate breaking C–H or C–D bonds cannot take place in the rate determining step.



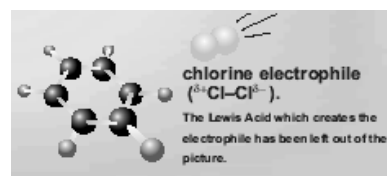


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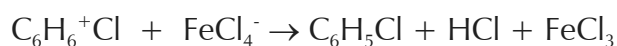
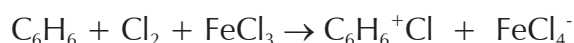
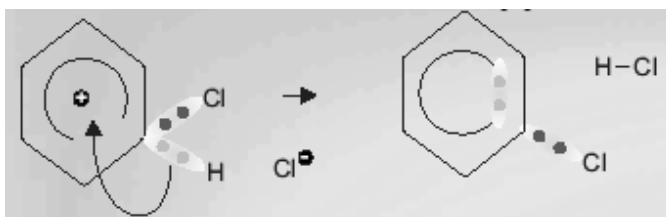
25 minutes **consolidation** and **summary**



Chlorine has little effect on benzene. Could a catalyst change it into an electrophile able to break into a benzene ring? What would the catalyst have to do to



the chlorine molecule? A 'Lewis Acid', an electron pair acceptor, can polarize chlorine into a powerful electrophile. The 'Lewis Acid' by pulling the bonding electrons away from one end of a chlorine molecule changes it into a powerful electrophile. Powerful enough to pull a pair of electrons out of a benzene ring.



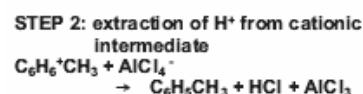
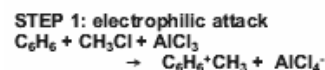
The  $\text{FeCl}_4^-$  anion extracts an  $\text{H}^+$  from the cationic intermediate. This forms  $\text{C}_6\text{H}_5\text{Cl}$  and  $\text{HCl}$  at the same time as regenerating the original Lewis Acid catalyst.

### Lesson 26.6 – Electrophilic Addition

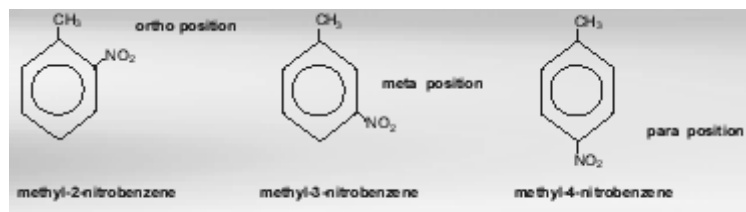
Present class notes 26.6a and 26.6b

15 minutes **introduction**

Ask student(s) to outline, with diagrams, the mechanism of electrophilic substitution with chloromethane ( $\text{CH}_3\text{Cl}$ ) rather than chlorine ( $\text{Cl}_2$ ) as the electrophile.



20 minutes **consolidation**

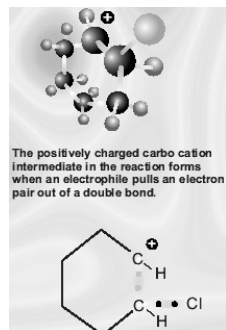


Ask students to work out the possible outcomes when further substitution occurs on a mono substituted ring (if each outcome was as likely as any other, 20% would happen at the 'para' position, 40% at the 'ortho' and

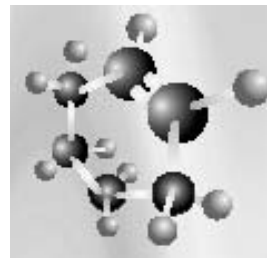
40% at the 'meta' position, since this does not happen it suggests there is an underlying mechanism directing substitution). Identify ortho/para and meta directing substituents and give an explanation for their action.

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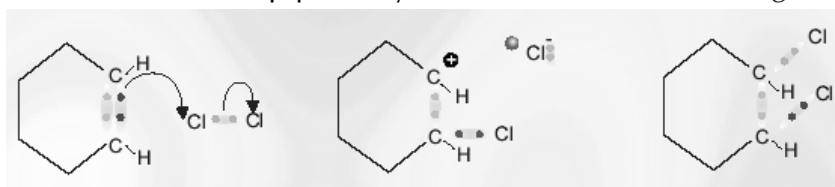
20 minutes **development demonstration**



Add bromine water (containing  $\text{Br}_2$  molecules) to samples of methyl benzene ( $\text{C}_6\text{H}_5\text{CH}_3$ ) and cyclohexene ( $\text{C}_6\text{H}_{10}$ ). Nothing much happens with methyl benzene but the reddish brown bromine water immediately loses its color on contact with cyclohexene ( $\text{Br}_2$  is used rather than  $\text{Cl}_2$  because the color change signifying reaction is more obvious). Lead discussion of observations to conclusion that since the bromine reacts much more readily with the double bond in cyclohexene (without a catalyst) than a benzene ring, it suggests a different reaction mechanism is involved, **addition rather than substitution**. What are the possibilities? A one step pathway with simultaneous breaking and making of bonds or a two step process through a intermediate? Ask students how they would gain evidence to choose



between the two (a 1,2 dihalide with a 'foreign' nucleophile would give evidence that it is a two step process with a carbocation intermediate). Lead to conclusion that the electron rich double bond induces a dipole in the halogen which initiates electrophilic attack.



5 minutes **summary**

- Electrophilic addition occurs when an electrophile bonds by pulling electrons out of a double (or triple) bond. A carbocation is formed as an intermediate in this type of reaction.

### Lesson 26.7– Investigation 23 – Reaction Mechanisms

This is a six-day investigation consisting of six separate experiments.

Assign students to complete lab work and write-up for each experiment separately.

See **Teacher Version** of student lab book for procedures, details, and discussion.

Review key safety considerations, chemical procedures, and concepts.

Before starting the series of investigations on reaction mechanisms in carbon chemistry students should spend some time researching the reactions they are going to carry out. They should plan how they intend to carry out the investigations and design tables to record their results. Once they have a clear idea of what they are investigating and how they intend to carry out their investigations they can be given the detailed procedures which list reactant quantities to use.

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### Teacher Notes: Experimental Procedures and Student Instructions

#### Experiment 1:

FREE RADICAL SUBSTITUTION Reaction of hexane with bromine

- 1 Put 2 cm<sup>3</sup> of hexane in each of two test tubes.
- 2 Add 1 DROP of bromine to each test tube.  
**(WEAR EYE PROTECTION AND WORK IN A FUME CUPBOARD)**
- 3 Use aluminium foil to make one of the test tubes light proof.
- 4 Stand the two test tubes side by side in bright sunlight (if unavailable a bright light will do) for 5 to 10 minutes.
- 5 Examine the tubes. Blow a little ammonia across the top of each test tube.

Record your observations and outline a mechanism for the reaction that took place

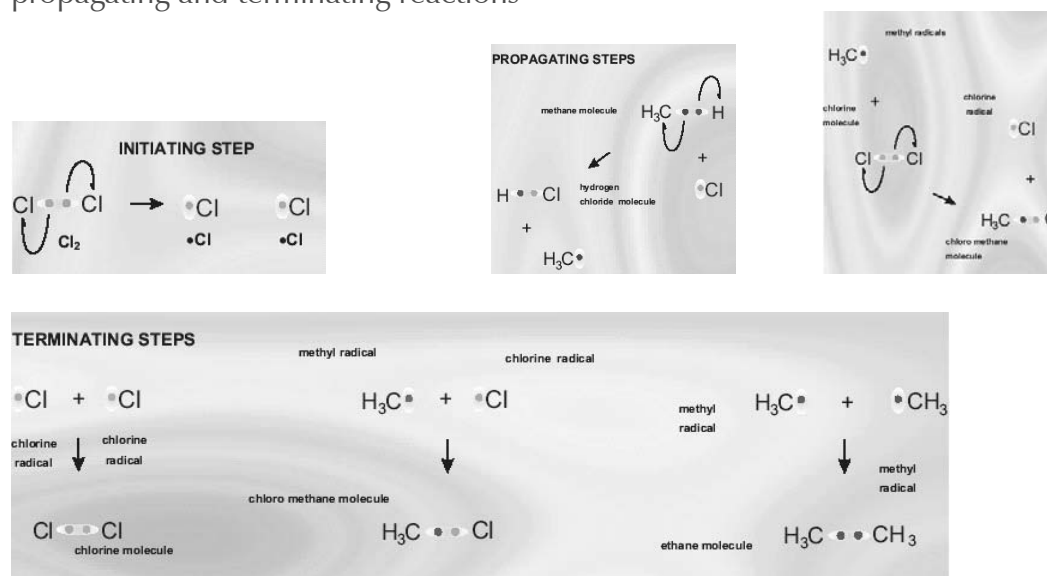
#### Experiment 1 – Teacher Notes Instructions, Explanations, and Answers

Work in a well ventilated laboratory !

Br<sub>2</sub> reacts with hexane (C<sub>6</sub>H<sub>12</sub>) when exposed to sunlight, the reddish brown Br<sub>2</sub> loses its color. The HBr can be identified with NH<sub>3</sub> (they react to form white fumes of NH<sub>4</sub><sup>+</sup>Br<sup>-</sup>)



the mechanism follows the same sequence as that for Cl<sub>2</sub> and CH<sub>4</sub> with initiating, propagating and terminating reactions



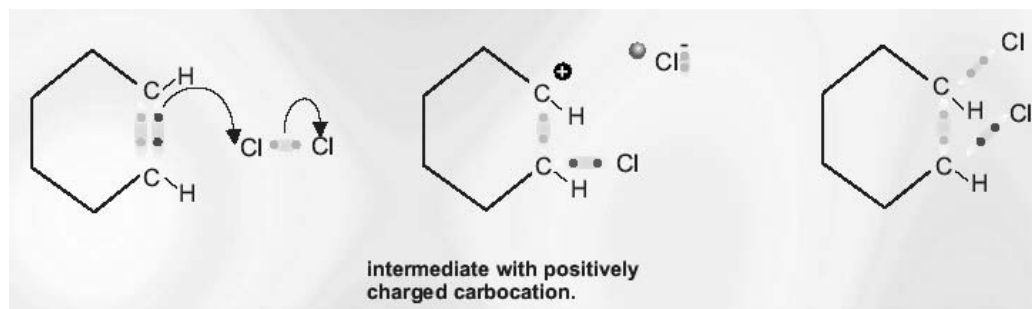
Both Br<sub>2</sub> and MnO<sub>4</sub><sup>-</sup> react on contact with cyclohexene (C<sub>6</sub>H<sub>10</sub>) (the latter oxidize alkenes to alkanols C=C + [O] → COH COH (detailed mechanism not required). Cyclohexane (C<sub>6</sub>H<sub>12</sub> and merthybenzene (C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>) only react slowly with Br<sub>2</sub> in sunlight, the alkane C in C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub> also undergoes free radical substitution. The benzene ring is unaffected

$$\text{Br}_2 + \text{C}_6\text{H}_{10} \rightarrow \text{C}_6\text{H}_{10}\text{Br}_2$$

## Chapter 26: Pathways in Organic Reaction Daily Lesson Plans

electrophilic addition

$\text{Br}_2$  adds on across the  $\text{C}=\text{C}$  in the same way as  $\text{Cl}_2$  with cyclohexene



### ELECTROPHILIC ADDITION

Reaction of hydrocarbons with bromine water and with acidified potassium manganate (V)

a) Add  $1 \text{ cm}^3$  of bromine water to separate  $1 \text{ cm}^3$  samples of:  
CYCLOHEXANE, CYCLOHEXENE, AND METHYLBENZENE.

Shake all four mixtures thoroughly.

b) Add  $1 \text{ cm}^3$  of dilute sulphuric acid and  $1 \text{ cm}^3$  of dilute potassium manganate (VII) to separate  $1 \text{ cm}^3$  samples of:  
CYCLOHEXANE, CYCLOHEXENE, AND METHYLBENZENE.

Shake all four mixtures thoroughly.

Record your observations and outline a mechanism for the reactions that have taken place:

### Experiment 2:

#### NUCLEOPHILIC SUBSTITUTION REACTIONS OF HALOGENOALKANES

Effect of the halogen atom on the rate of hydrolysis

Set up three labelled test tubes as described in the following table:

TEST TUBE 1	TEST TUBE 2	TEST TUBE 3
$1 \text{ cm}^3$ ethanol	$1 \text{ cm}^3$ ethanol	$1 \text{ cm}^3$ ethanol
2 drops 1-chlorobutane	2 drops 1-bromobutane	2 drops 1-iodobutane

- 1 Stand the test tubes in a beaker of water at about  $50^\circ\text{C}$ .
- 2 Put a test tube containing  $5 \text{ cm}^3$  of  $0.1 \text{ mol dm}^{-2}$  silver nitrate in the same beaker.
- 3 Leave the test tubes for about 10 minutes.
- 4 Add  $1 \text{ cm}^3$  of silver nitrate solution to each of the test tubes and note the time.
- 5 Shake each test tube to mix the contents.
- 6 Observe the test tubes over the next five minutes or so.

Record your observations and outline a mechanism for the reactions that have taken place:

## Chapter 26: Pathways in Organic Reaction Daily Lesson Plans

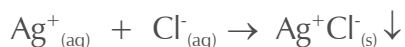
### Experiment 2 - Teacher Notes - Instructions, Explanations, and Answers

The effect of the halogen as a 'leaving' group is investigated

Note that water molecules are acting as the nucleophile, the  $\text{Ag}^+$  ions are present to precipitate with the leaving halide ions, the  $\text{NO}_3^-$  ions are spectators.



1-chlorobutane



the appearance of the precipitate allows the reaction times to be compared

$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{I}$  1-iodobutane reacts fastest ; 1-chlorobutane the slowest

### Experiment 3:

#### NUCLEOPHILIC SUBSTITUTION REACTIONS OF HALOGENOALKANES

Effect of the structure of the carbon skeleton on the reaction mechanism and reaction rate.

Set up three labelled test tubes as described in the following table:

TEST TUBE 1	TEST TUBE 2	TEST TUBE 3
1 cm <sup>3</sup> ethanol	1 cm <sup>3</sup> ethanol	1 cm <sup>3</sup> ethanol
2 drops 1-bromobutane	2 drops 2-bromobutane	2 drops 2-bromo-2-methylpropane

1 Add 1 cm<sup>3</sup> of silver nitrate solution to each of the test tubes and note the time.

2 Shake each test tube to mix the contents.

3 Observe the test tubes over the next five minutes or so.

Record your observations and outline a mechanism for any reactions that have taken place:

### Experiment 3: Instructions, Explanations, and Answers

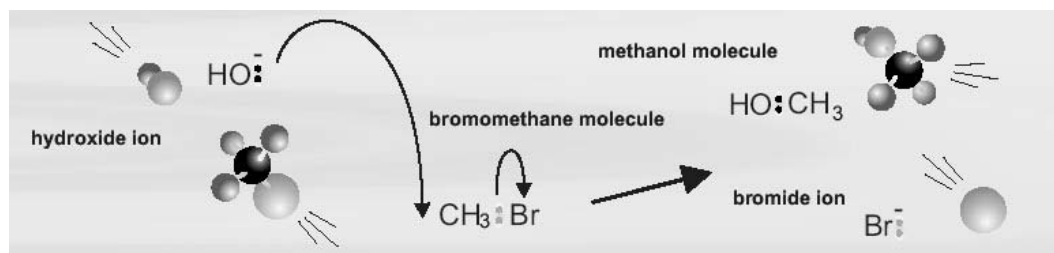
The effect of the carbon skeleton on rate is investigated

$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$  1-bromobutane primary C  
slowest

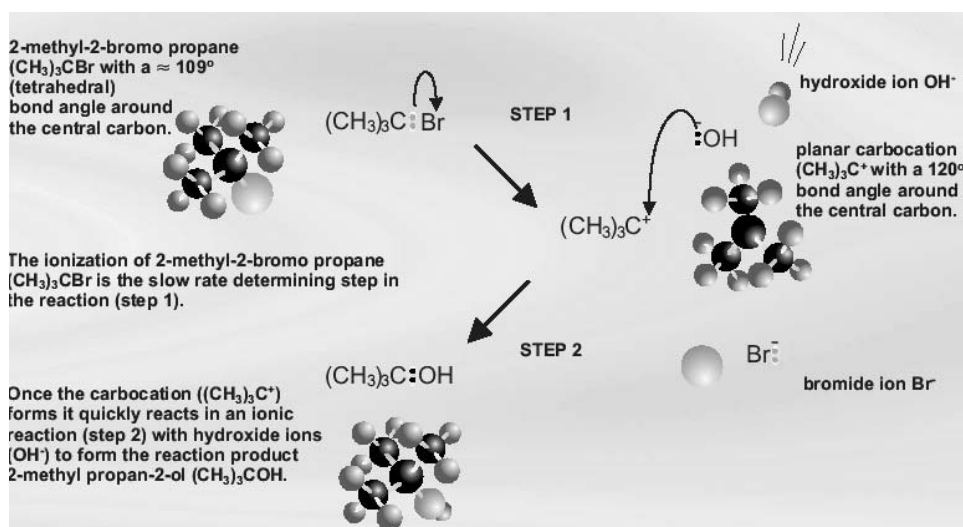
$\text{CH}_3\text{CH}_2\text{CHBrCH}_3$  2-bromobutane secondary C

$\text{CH}_3\text{CBr}(\text{CH}_3)\text{CH}_3$  2-bromo-2-methylpropane tertiary C fastest

(nucleophilic substitution on primary carbon  $\text{S}_{\text{N}}2$  mechanism (when  $\text{H}_2\text{O}$  acts as nucleophile after substitution it loses a  $\text{H}^+$   $\text{CH}_3\text{OH}_2^+ \rightarrow \text{CH}_3\text{OH} + \text{H}^+$ )



nucleophilic substitution on tertiary carbon  $\text{S}_{\text{N}}1$  mechanism



#### Experiment 4:

#### NUCLEOPHILIC SUBSTITUTION REACTIONS OF HALOGENOALKANES

Effect of solvent on the reaction mechanism and the reaction rate

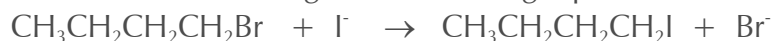
- 1 Dissolve 1 gram of sodium iodide in 15 cm<sup>3</sup> of propanone.
- 2 Put 5 cm<sup>3</sup> of this iodide solution into each of three labelled test tubes.
- 3 Stand the test tubes in a beaker of water at 35°C.
- 4 Leave the test tubes 10 minutes.
- 5 Noting the time;
  - (i) add 8 drops of 1-bromobutane to the first test tube,
  - (ii) add 8 drops of 2-bromobutane to the second test tube,
  - (iii) add 8 drops of 2-bromo-2-methylpropane to the third test tube,
- 6 Observe the test tubes over the next five minutes or so.

Record your observations and outline a mechanism for the reactions that have taken place:

#### Experiment 4 - Teacher Notes – Instructions, Explanations, and Answers

Changing the solvent reverses the effect of carbon skeleton on reaction rate

In a non aqueous solvent, such as propanone, iodide ions will substitute the bromine in a bromoalkane according to the following equation:



The iodide ions can be supplied by sodium iodide. Sodium bromide (Na<sup>+</sup>Br<sup>-</sup>), unlike sodium iodide, is insoluble in propanone, hence the appearance of the precipitate can be used to compare reaction times

CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> Br	1-bromobutane	primary C	fastest
CH <sub>3</sub> CH <sub>2</sub> CHBrCH <sub>3</sub>	2-bromobutane	secondary C	
CH <sub>3</sub> CBr(CH <sub>3</sub> )CH <sub>3</sub>	2-bromo-2-methylpropane	tertiary C	slowest

## Chapter 26: Pathways in Organic Reaction Daily Lesson Plans

### Experiment 5:

#### NUCLEOPHILIC ADDITION

Condensation reactions of carbonyl compounds

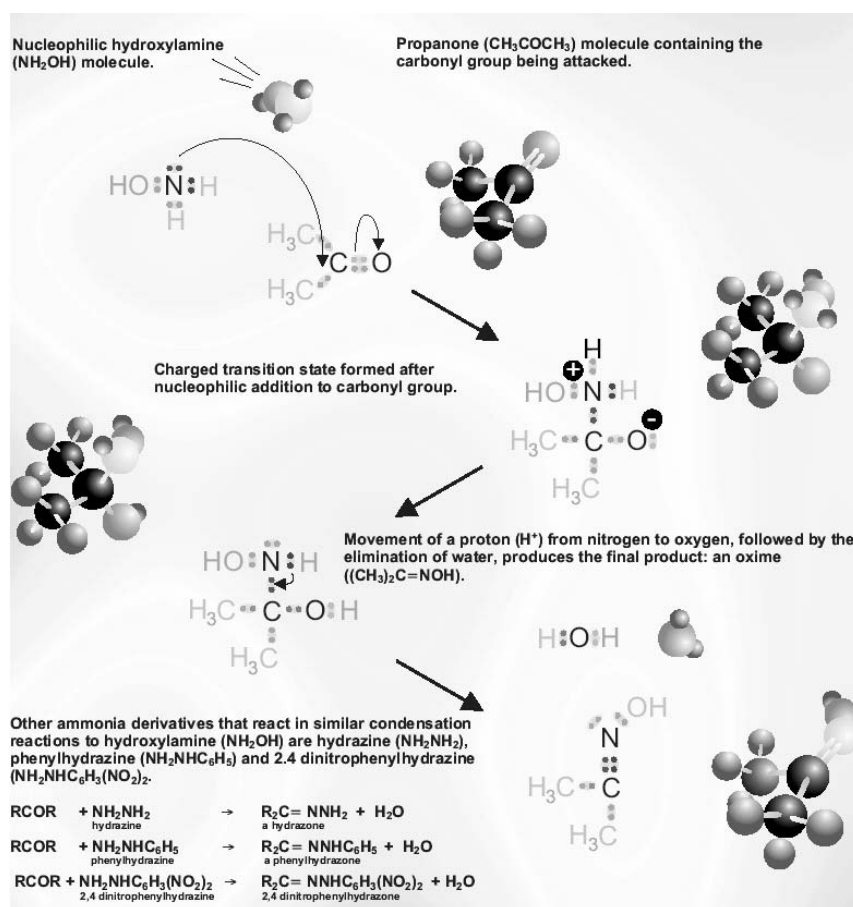
#### PREPARATION OF PROPANONE 2,4-DINITROPHENYLHYDRAZONE

Add 5 cm<sup>3</sup> of 2,4-dinitrophenylhydrazine solution to 3 drops of propanone. If crystals do not form add a little 2 mol dm<sup>-3</sup> sulphuric acid, warm the mixture and cool in ice water bath. Dry the crystals between filter papers. Determine their melting point and compare with the accepted value of 128°C for the melting point of propanone 2,4-dinitrophenylhydrazone. Record your observations and outline a mechanism for the reaction that took place:

### Experiment 5 – Teacher Notes, Instructions, Explanations, and Answers

This introduces student to using melting point determination as indication of purity, a sudden sharp change of shape indicating a single substance in the sample, a wider range a mixture.

Mechanism for nucleophilic addition (substitute  $-\text{NHC}_6\text{H}_3(\text{NO}_2)_2$  for the OH in  $\text{NH}_2\text{OH}$  for the formula of 2,4-dinitrophenylhydrazine)



## Chapter 26: Pathways in Organic Reaction Daily Lesson Plans

### Experiment 6:

#### ELECTROPHILIC SUBSTITUTION

Preparation and purification of methyl 3-nitrobenzoate.

Preparation: (WEAR EYE PROTECTION)

- 1 Weigh out 2.7 grams of methyl benzoate (a liquid) into a small conical flask and then dissolve it in 5 cm<sup>3</sup> of concentrated sulphuric acid. When the solid has dissolved, cool the mixture in ice.
- 2 Prepare the nitrating mixture by carefully adding 2 cm<sup>3</sup> of concentrated sulphuric acid to 2 cm<sup>3</sup> of concentrated nitric acid and then cool this mixture in ice.
- 3 Add the nitrating mixture drop by drop from a teat pipette to the solution of methyl benzoate. Stir with a thermometer and keep the temperature below 10°C.
- 4 When the addition is complete allow the mixture to stand at room temperature for 15 minutes.
- 5 Pour the mixture on to about 25 grams of crushed ice. Stir until all the ice has melted and crystalline methyl 3-nitrobenzoate has formed.

Purification:

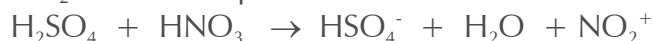
- 6 Filter the crystals using a Buchner funnel, wash them thoroughly with cold water and then transfer to a small beaker.
- 7 Warm 15 cm<sup>3</sup> of ethanol to about 50°C  
USE A WATER BATH AND KEEP THE ETHANOL AWAY FROM NAKED FLAMES
- 8 Dissolve the crystals in the minimum volume of this hot ethanol.
- 9 Allow the solution to cool to room temperature and then immerse in iced water to complete the crystallization of methyl 3-nitrobenzoate.
- 10 Filter the crystals, dry them between filter papers and weigh them. Record the mass obtained and determine the melting point of your product (pure methyl 3-nitrobenzoate melts at 77.5°C).
- 11 Comment on the percentage yield and the purity of your product.
- 12 Outline a mechanism for the reaction that took place.

### Experiment 6 - Teacher Notes - Instructions, Explanations, and Answers

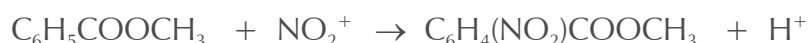
An organic synthesis where the melting point of the product indicates how well the students followed the experimental procedure (allowing the reaction mixture to rise above 10°C is likely to produce more than the mono nitro substituted product). This synthesis will also allow students to compare their yield to the theoretical yield and comment on any discrepancy.

Electrophilic substitution (mechanism shown for C<sub>6</sub>H<sub>6</sub> methyl benzoate is C<sub>6</sub>H<sub>5</sub>COOCH<sub>3</sub> the -COOCH<sub>3</sub> group activates the benzene ring but does not affect the mechanism)

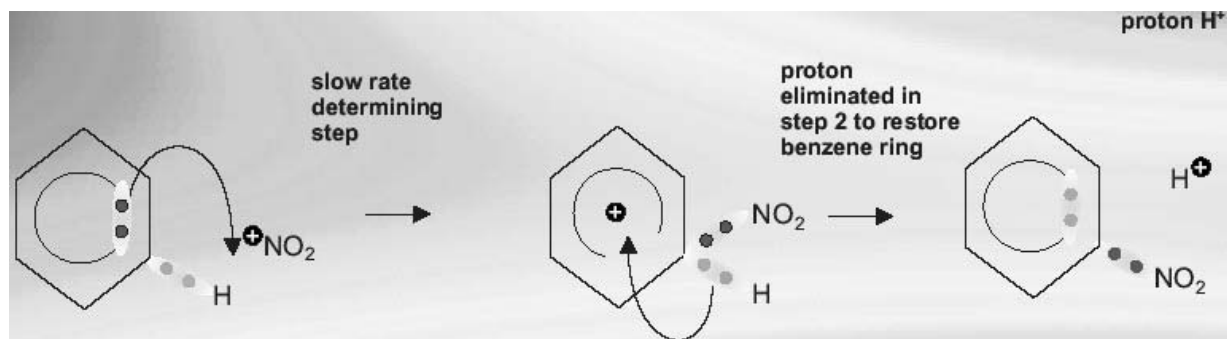
formation of nitronium ion NO<sub>2</sub><sup>+</sup> the electrophile



reaction



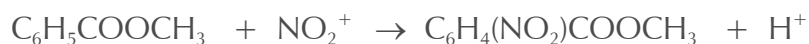




### Experiment 6: Teacher Notes and Student Instructions - Calculating the % yield

Methyl benzoate  $\text{C}_6\text{H}_5\text{COOCH}_3$   $(12 \times 8) + (16 \times 2) + (8 \times 1) = 136 \text{ grams mol}^{-1}$   
 $\therefore$  the 2.7 grams suggested in the experimental procedure contains  $\approx 2.0 \times 10^{-2}$  mols of methyl benzoate molecules)

$\text{C}_6\text{H}_4(\text{NO}_2)\text{COOCH}_3$   $(12 \times 8) + (16 \times 4) + (7 \times 1) + 14 = 181 \text{ grams mol}^{-1}$



$\therefore$  136 grams of  $\text{C}_6\text{H}_5\text{COOCH}_3$  with a 100% yield would produce 181 grams of  $\text{C}_6\text{H}_4(\text{NO}_2)\text{COOCH}_3$

$\therefore$  if 2.71 grams of  $\text{C}_6\text{H}_5\text{COOCH}_3$  ( $2.0 \times 10^{-2}$  mols of molecules) would theoretically produce  $181 \times 2 \times 10^{-2} = 3.62$  grams of  $\text{C}_6\text{H}_4(\text{NO}_2)\text{COOCH}_3$

$\therefore$  for example if only 3.10 grams of  $\text{C}_6\text{H}_4(\text{NO}_2)\text{COOCH}_3$  were produced % yield =  $(3.10 \times 100) \div 3.62 = 85.6\%$

In this reaction if the temperature is allowed to rise over  $10^\circ\text{C}$  it is likely than the products could include the di nitro substituted derivative. These could make the yield appear to be greater than 100%!

di nitro derivative  $\text{C}_6\text{H}_3(\text{NO}_2)_2\text{COOCH}_3$

$(12 \times 8) + (16 \times 6) + (6 \times 1) + 28 = 226 \text{ grams mol}^{-1}$

## Chapter 26: Pathways in Organic Reaction Daily Lesson Plans

### Assessment Criteria: students should

#### Design

answer the questions in the planning document before starting the experiments

#### Data collection and processing

be careful when handling reactants, note and relate the appearance of reactants and products to the reactions taking place, design a table to record their observations, be willing to redo suspect results, be able to relate observations to the reactions taking place, understand that a substance's melting point is an indication of purity, be able to calculate a percentage yield

#### Conclusion and evaluation

Draw diagrams showing the different reaction mechanisms for the reactions they have carried out

### Lesson 26.8 – Investigation 23 continued

Today, students conduct experiment two of the series.

See **Teacher Version** of student lab book for procedures, details, and discussion.

Review key safety considerations, chemical procedures, and concepts.

Students write-up today's experiment in class or as homework if necessary.

### Lesson 26.9 – Investigation 23 – continued

Today, students conduct experiment three of the series.

See **Teacher Version** of student lab book for procedures, details, and discussion.

Review key safety considerations, chemical procedures, and concepts.

Students write-up today's experiment in class or as homework if necessary.

### Lesson 26.10 – Investigation 23 continued

Today, students conduct experiment four of the series.

See **Teacher Version** of student lab book for procedures, details, and discussion.

Review key safety considerations, chemical procedures, and concepts before beginning.

Students write-up today's experiment in class or as homework if necessary.

## Chapter 26: Pathways in Organic Reaction Daily Lesson Plans

### Lesson 26.11– Investigation 23 – continued

Today, students conduct experiment five of the series.

See **Teacher Version** of student lab book for procedures, details, and discussion.

Review key safety considerations, chemical procedures, and concepts.

Students write-up today's experiment in class or as homework if necessary.

### Lesson 26.12– Investigation 23 continued

Today, students conduct experiment six of the series.

See **Teacher Version** of student lab book for procedures, details, and discussion.

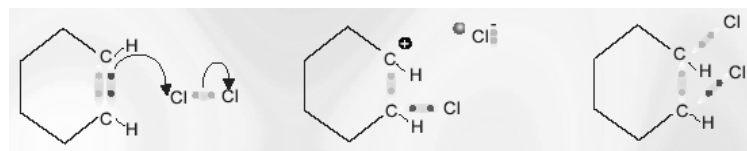
Review key safety considerations, chemical procedures, and concepts.

Students write-up today's experiment in class or as homework if necessary.

### Lesson 26.13 – Addition of Hydrogen Halides; Relative Rates of Addition

Present class notes 26.7a to 26.7c

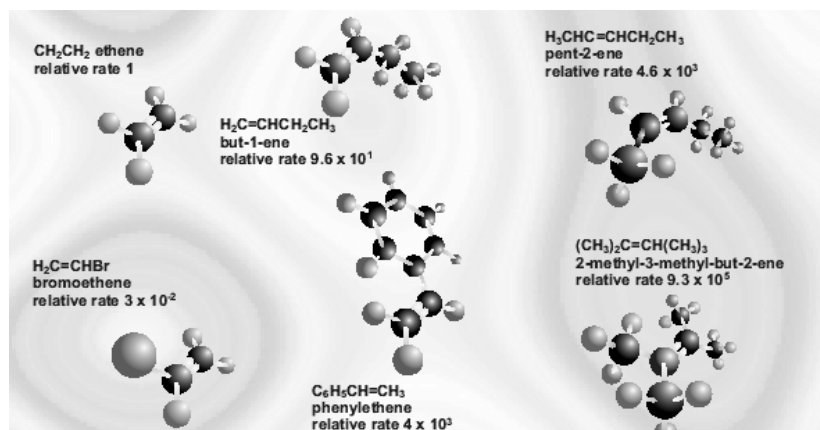
10 minutes **introduction**



Ask students to draw a diagram outlining the electrophilic addition of  $\text{Cl}_2$  to  $\text{C}_6\text{H}_{10}$ . Note how the bond angles on the carbon atoms change. Demonstrate with model.

20 minutes **development**

Comparing the relative rates of addition on substituted alkenes gives evidence for the proposed cationic intermediate in electrophilic addition. Ask students to predict the effect of electron releasing methyl groups and electron withdrawing halogens on the stability of the cationic intermediate and hence on the reaction rate.



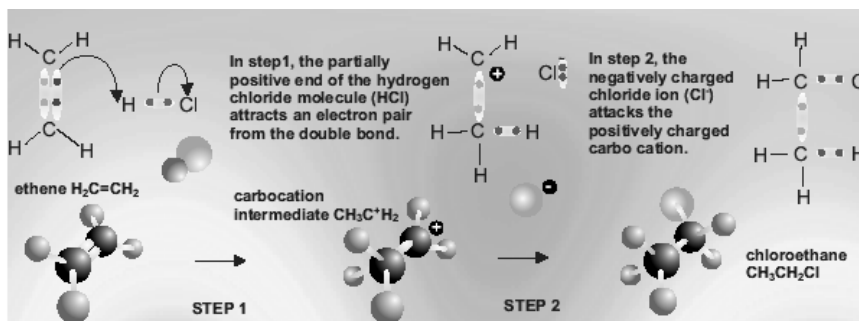
**TOK:** This could be discussed as an example of the use of the language of chemistry as a tool to classify and distinguish between different structures.

## Chapter 26: Pathways in Organic Reaction Daily Lesson Plans

### 25 minutes consolidation

Use models to outline the addition of hydrogen chloride (HCl) to ethane ( $C_2H_4$ ). Note the change in bond angles. Now ask students to do the same for the addition of

hydrogen chloride (HCl) to propene ( $C_3H_6$ ). Lead to realization that in this case there are two possible outcomes;  $CH_3CH_2CH_2Cl$  or  $CH_3CHClCH_3$ . To choose between the two, ask students to consider the stability of the cationic intermediate in both reactions (the cationic intermediate next to the electron releasing methyl group  $CH_3CH^+CH_3$  should be more stable and will thus be favored). This leads to the conclusion that the product is  $CH_3CHClCH_3$  rather than  $CH_3CH_2CH_2Cl$ . Ask students to formulate a rule to be used when predicting the product formed when a hydrogen halide (or similar molecule) adds onto an asymmetrical alkene. Lead to statement of **Markownikov's Rule**.



### 5 minutes Summary

Electrophilic addition occurs when an electrophile bonds by pulling electrons out of a double (or triple) bond. A carbo cation is formed as an intermediate in this type of reaction.

## Lesson 26.14 – Radical Reactants and Radical Substitution

Review chapter 26 study questions 5 and 6

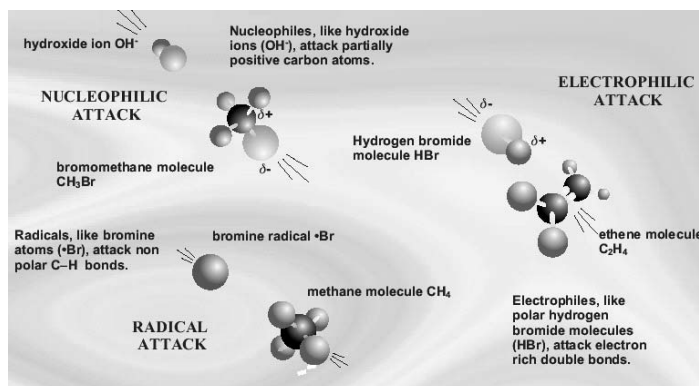
Homework – assign chapter 26 study question 7

Present class notes 26.8a and 26.8b

### 10 minutes Introduction

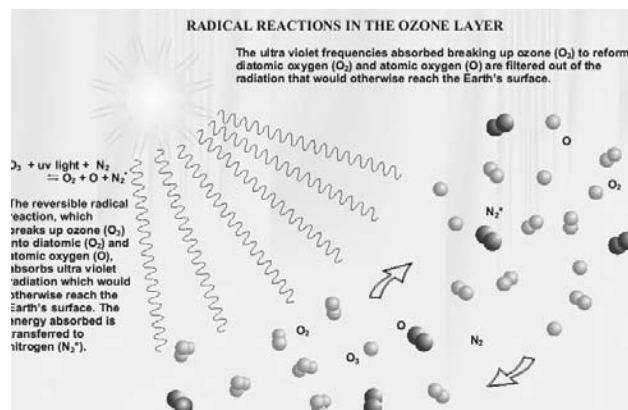
Summarize **addition** and **substitution** reactions with **electrophiles** and **nucleophiles**. Consider bonds breaking homolytically and heterolytically, lead discussion to the formation of reactive **free radicals**.

**TOK:** This could be discussed as an example of the use of the language of chemistry as a tool to classify and distinguish between different reactants.

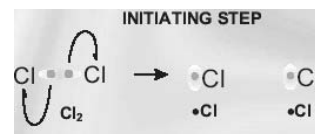


## Chapter 26: Pathways in Organic Reaction Daily Lesson Plans

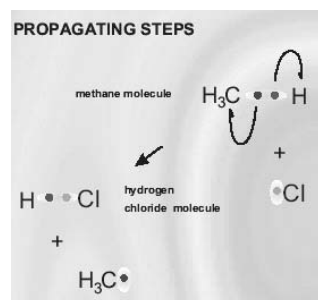
### 20 minutes **development**



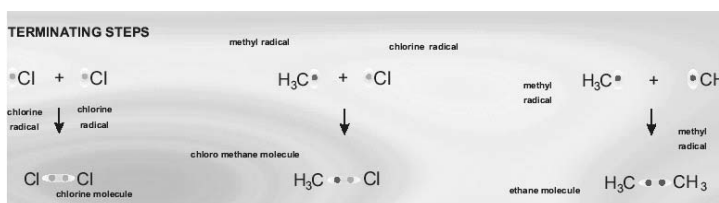
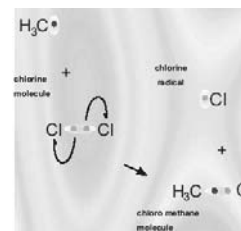
Introduce radical reactions via the role of ozone in absorbing uv radiation in the stratosphere. Mention radiation induced radical reactions can damage biological molecules like DNA. Lead discussion to the light induced homolytic fission and the reactivity of halogens. **Demonstrate** by adding bromine to two samples of cyclohexane, expose one to sunlight, keep the other covered.



### 25 minutes **consolidation**



Ask students to draw the result of a chlorine atom (a radical) attacking a carbon hydrogen bond. Identify the **methyl radical** and emphasize that a chain reaction has been set up because the radical produced can then attack another chlorine molecule to produce a chlorine radical to **propagate** the reaction. Ask students to consider that if this is the case why does the reaction initiated by a single photon come to a halt after a couple of million chloromethane molecules have been produced and leaving much of the methane in the original mixture unreacted? Lead students to conclusion that not all radicals react to produce another radical and so to identifying the **terminating** steps.



### 5 minutes **Summary**

- Alkanes undergo free radical substitution when they react with halogens in the presence of sunlight.
- Radical reactions can take place very rapidly. This is because once initiated further 'shots' of activation energy are not needed to propagate the reaction.

### **Lesson 26.15 – Polymerization**

Review chapter 26 study question 7

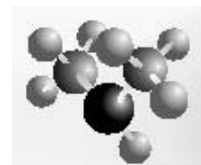
Homework – assign chapter 26 study question 8

Present class notes 26.9a

## Chapter 26: Pathways in Organic Reaction Daily Lesson Plans

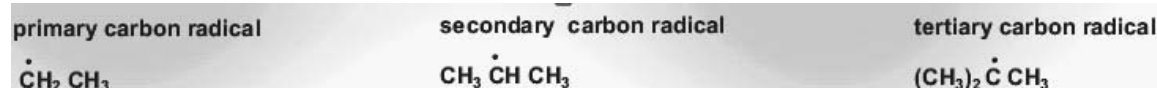
### 15 minutes **introduction**

Review **free radical substitution** by asking students to outline the **initiating**, **propagating** and **terminating** steps for the free radical substitution of ethane and propane. Ask students to predict which of the carbon radicals produced is the most stable (electron releasing methyl groups stabilize radicals) and how this could effect reaction rates.



### 20 minutes **development**

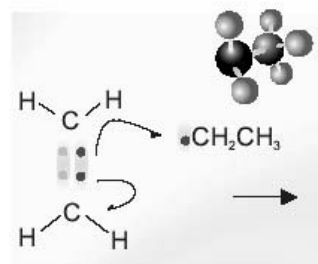
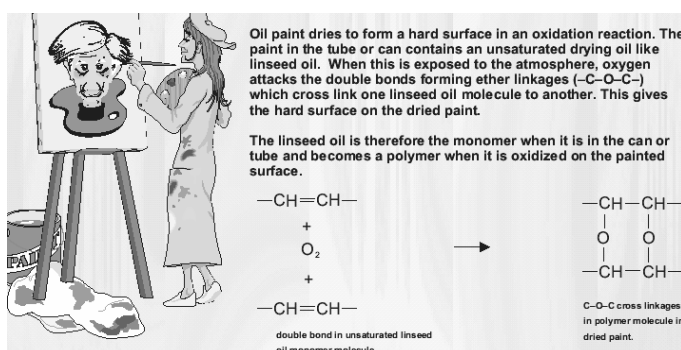
Consider the relative stabilities of **primary**, **secondary** and **tertiary** radicals.



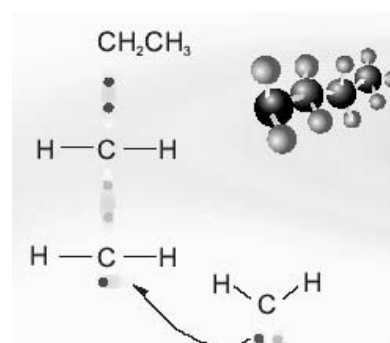
Emphasize the bond angles on the carbon radical (not planar as the unpaired electron repels). Lead discussion to the other factors which affect reaction rate: reactivity of halogen and strength of carbon hydrogen bonds. Use opportunity to mention that C-H bond strengths differ slightly in different environments; hence the C-H bond energy given in data books is an average.

### 20 minutes **consolidation**

Mention that 'aging' or slow oxidation involves free radical intermediates. Such reactions occur when paints dry, fats go rancid, rubber perishes and DNA is damaged. Include the role of anti oxidants in food and why they are



added to carbon compounds (antioxidants protect by reacting preferentially with free radicals). Link to auto oxidation in polymerization reactions. Ask students to predict what could happen when a carbon radical attacks a double bond. Lead to



description of reactions as initiating, propagating and terminating.

### 5 minutes **Summary**

- Radical addition (e.g. in polymerization) takes place when a free radical attacks a double bond to make a new C-C bond at the same time as generating a new radical to propagate the reaction.

## Chapter 26: Pathways in Organic Reaction Daily Lesson Plans

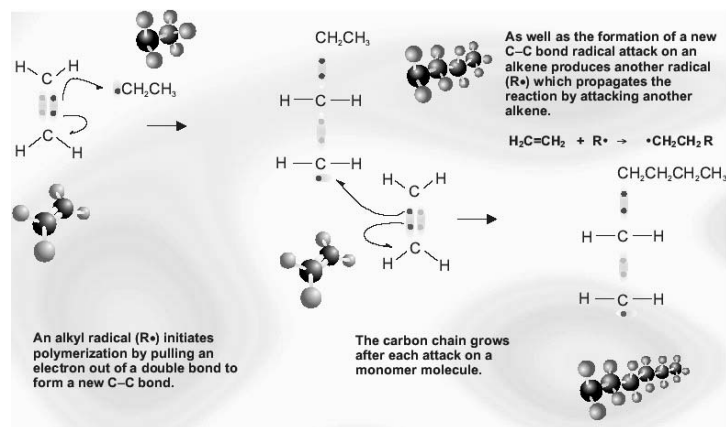
### Lesson 26.16 – Elimination versus Substitution

Review chapter 26 study questions 8

Homework – assign chapter 26 study question 9

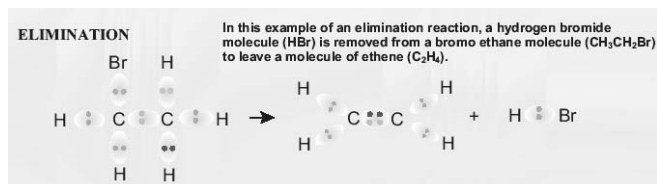
Present class notes 26.10a

#### 20 minutes introduction

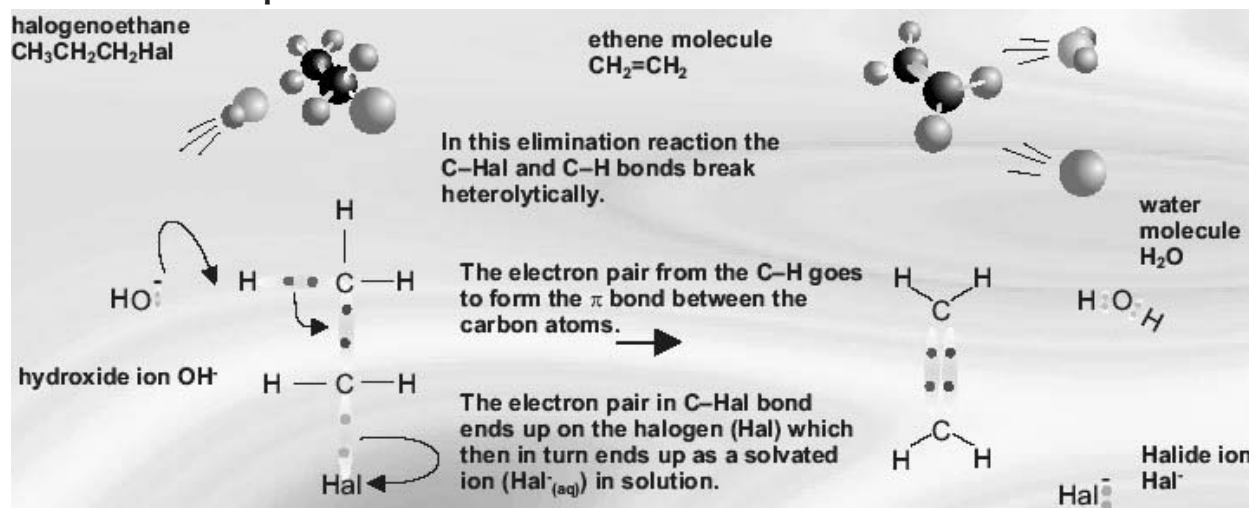


Use **radical addition** in polymerization to summarize the **initiating**, **propagating** and **terminating** steps in free radical reactions. Mention the way polymer chemists, by experimenting with a variety of conditions, produce polymers with the chain lengths and combinations to give a polymer with a desired set of properties. Remind students that there are only three

ways in which carbon compounds can react; **addition**, **substitution** and **elimination**. Ask students to predict the distinguishing feature of the product of an elimination reaction (multiple bond).



#### 25 minutes development



Ask students to propose an alternative (to nucleophilic substitution) when a hydroxide ion attacks a halogenoalkane. What would happen if the hydroxide ion, instead of acting as a nucleophile, acted as a base and pulled a proton out of a C-H bond?

Describe as an **Elimination Bimolecular (E<sub>2</sub>) mechanism**.

## Chapter 26: Pathways in Organic Reaction Daily Lesson Plans

Outline the experimental evidence for the proposed mechanism: the reaction is 2<sup>nd</sup> (rate =  $k[\text{CH}_3\text{CH}_2\text{Br}][\text{OH}^-]$ ) and experiments comparing the rates of elimination of 'ordinary' and 'deuterium' labeled halogenoalkanes confirm that a C-H bond breaks in the rate determining step. Discuss the role of the solvent in determining whether elimination or substitution takes place.

15 minutes **summary**

- The reactions carbon compounds undergo can be classified as **substitution, addition or elimination**.
- The reactants attacking carbon compounds as **electrophiles, nucleophiles or free radicals**

### Lesson 26.17 – Test One 2<sup>nd</sup> Quarter

Year two – First test of the second quarter

### Lesson 26.18 – Correcting Test

In-class exam corrections.

Complete remaining items as homework as necessary.