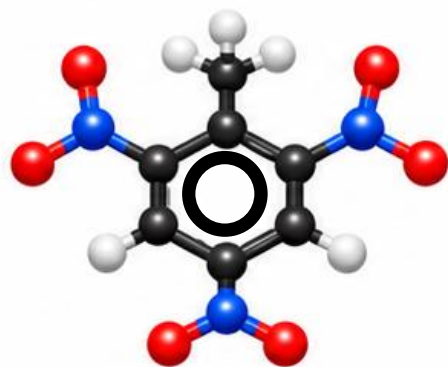
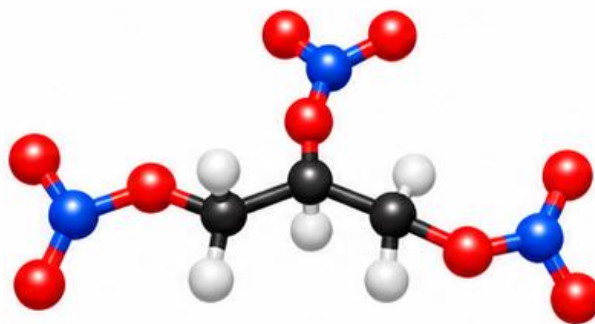


Reaction Chemistry of Energetic Materials

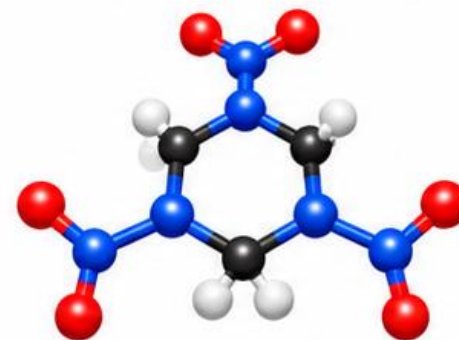
How molecular structure controls
reaction pathways and product formation



TNT
(2,4,6-trinitrotoluene)
 $C_7H_5N_3O_6$



Nitroglycerine
 $C_3H_5N_3O_9$



RDX
 $C_3H_6N_6O_6$

Where Session 1 sits in the OME lifecycle



Manufacture



Storage



Use



Disposal

**Molecular
structure**



**Reaction
pathway**



**Product
composition**

S1 question: How does molecular structure control what we make?

What leaves Manufacture becomes the starting material for Storage, Use and Disposal.

Explain why reaction chemistry belongs at the beginning of Advanced Chemistry of OME.

Today's route

From molecular structure to the composition of the material leaving manufacture.

	Chapter	Question we are answering
1	Reading molecular structure	What is actually in the molecule?
2	Structure controls reaction pathway	How does molecular structure determine how it reacts?
3	One reaction changes the next	How do substituents change reactivity and where the next reaction occurs?
4	From predicted product to manufactured mixture	Do we actually make only the product we predicted?
5	Different structures, different nitration chemistry	Does "nitration" mean the same reaction for every energetic material?
6	From reaction to evidence	How do we establish what we actually made?



Session 1 outcome:

connect molecular structure to the composition of the material leaving manufacture.

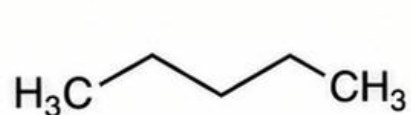


Organic chemistry: what are we studying?

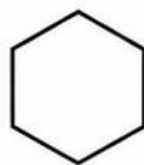
Organic chemistry examines carbon compounds: how atoms are connected and how that connectivity affects chemical behaviour.

1 Carbon forms molecular frameworks

Carbon can form chains, rings and other skeletons, providing the framework of the molecule.



Open chain



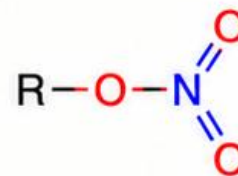
Ring

2 Other atoms and groups change the chemistry

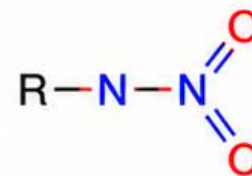
Atoms such as N and O, and the groups they form, can strongly alter chemical behaviour.



Nitro group



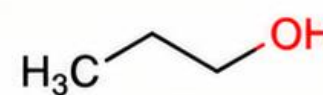
Nitrate ester



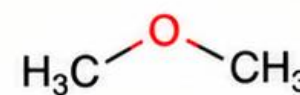
Nitramine

3 Connectivity matters

The same atoms connected differently can produce different chemical behaviour.



Ethanol
(alcohol)



Dimethyl ether
(ether)

Why this matters for OME

Energetic materials are not defined simply by which elements they contain. **How those atoms are connected determines functionality, reaction pathways and ultimately the products formed.**

What information can we read from a structure?

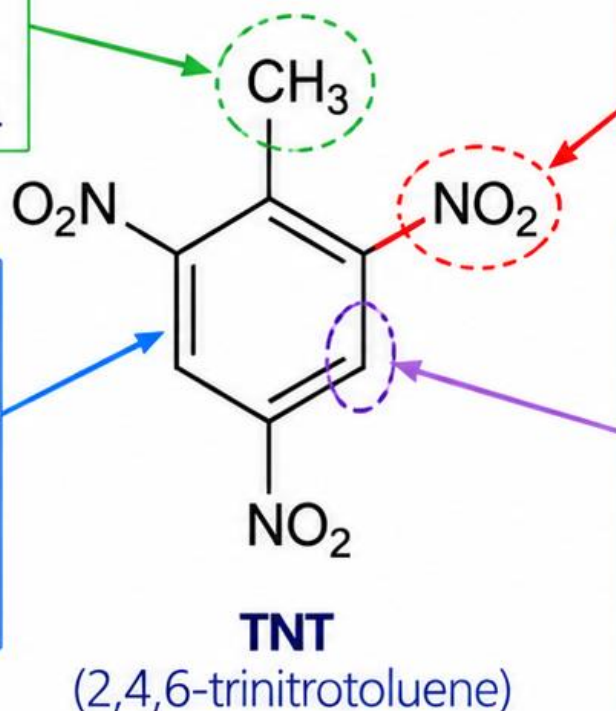
A molecular structure tells us more than just the name. We can extract information that helps us predict how the molecule might react.

1. Connectivity

Which atoms are directly bonded?
The $-\text{CH}_3$ group is bonded to the aromatic ring carbon.

3. Local environment

What surrounds the reaction sites?
Each $-\text{NO}_2$ is attached to an sp^2 carbon in an aromatic ring, with two other substituents present.



2. Functional groups

What chemically distinctive groups are present?
Three nitro ($-\text{NO}_2$) groups and one methyl ($-\text{CH}_3$) group.

4. Potential reactivity

Which parts of the molecule might control the reaction pathway?
The electron-withdrawing $-\text{NO}_2$ groups and the electron-donating $-\text{CH}_3$ group influence where and how the molecule reacts.

Key information from a structure

1. Connectivity

Which atoms are directly bonded?

2. Functional groups

What chemically distinctive groups are present?

3. Local environment

What surrounds the reaction sites?

4. Potential reactivity

Which parts of the molecule might control the reaction pathway?

**At Level 6, the task is not simply to recognise a structure.
It is to use the structure to make a chemical prediction.**

Move students from *recognising* a chemical structure to *interrogating* one chemically.

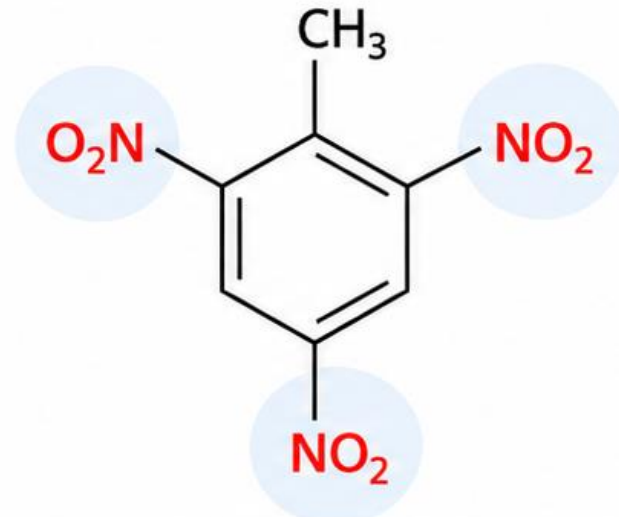
Same $-\text{NO}_2$ unit, different molecular environments

Ch1

Three energetic materials containing the $-\text{NO}_2$ group.

TNT

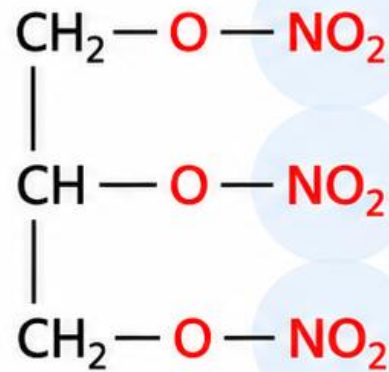
Nitro compound



$-\text{NO}_2$ attached directly to carbon
($\text{C}-\text{NO}_2$)

Nitroglycerine

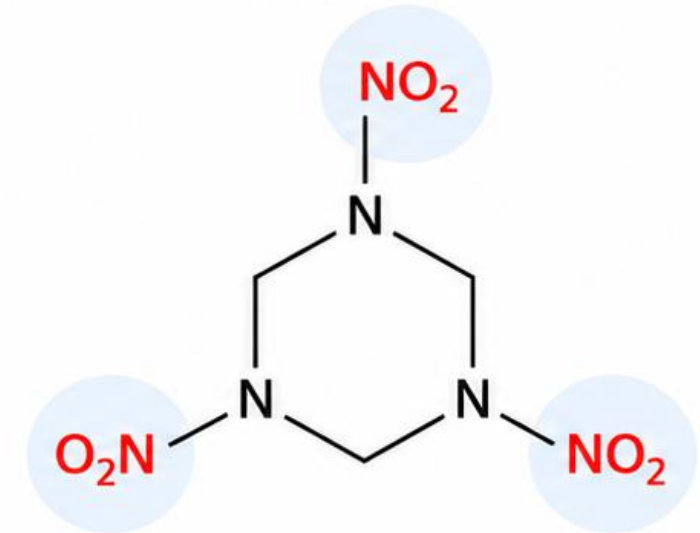
Nitrate ester



$-\text{NO}_2$ attached through oxygen
($\text{C}-\text{O}-\text{NO}_2$)

RDX

Nitramine



$-\text{NO}_2$ attached to nitrogen
($\text{C}-\text{N}-\text{NO}_2$)

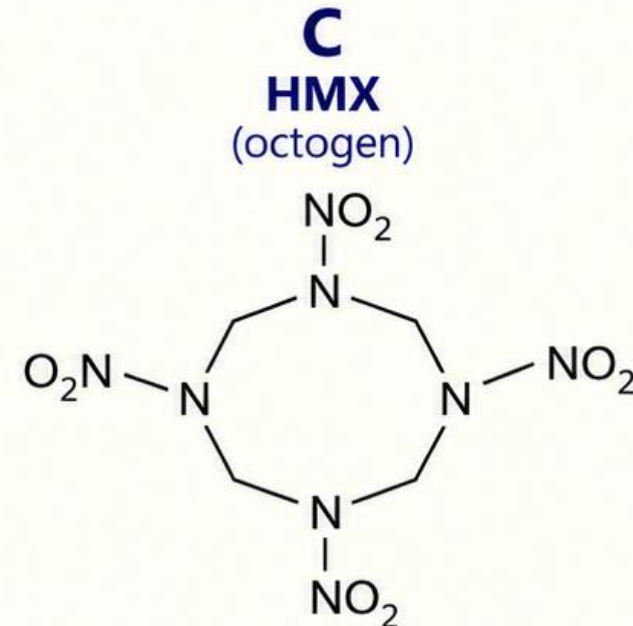
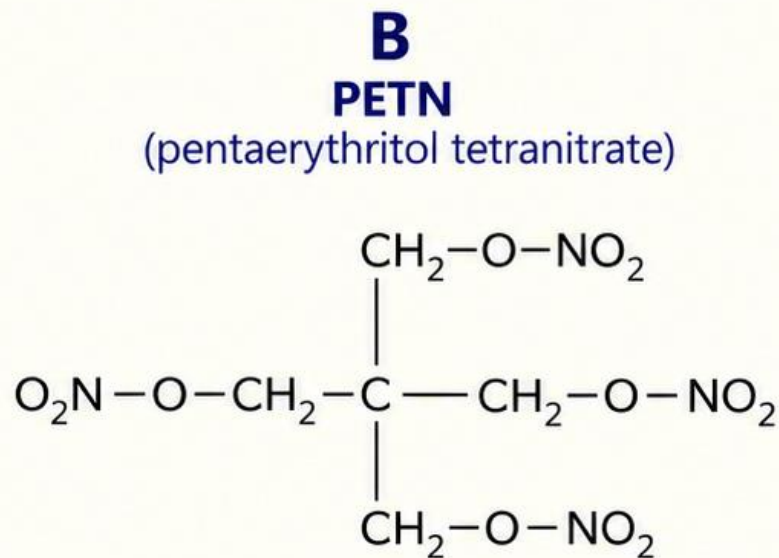
Key question:

Why might these different connectivities lead to different chemical behaviour, even though all three materials contain C, H, N and O?

Introduce the central conceptual distinction between nitro compounds, nitrate esters and nitramines.

Activity: same NO₂ unit, same chemistry?

Consider the three energetic materials below. Each contains nitrogen–oxygen functionality with different connectivity.

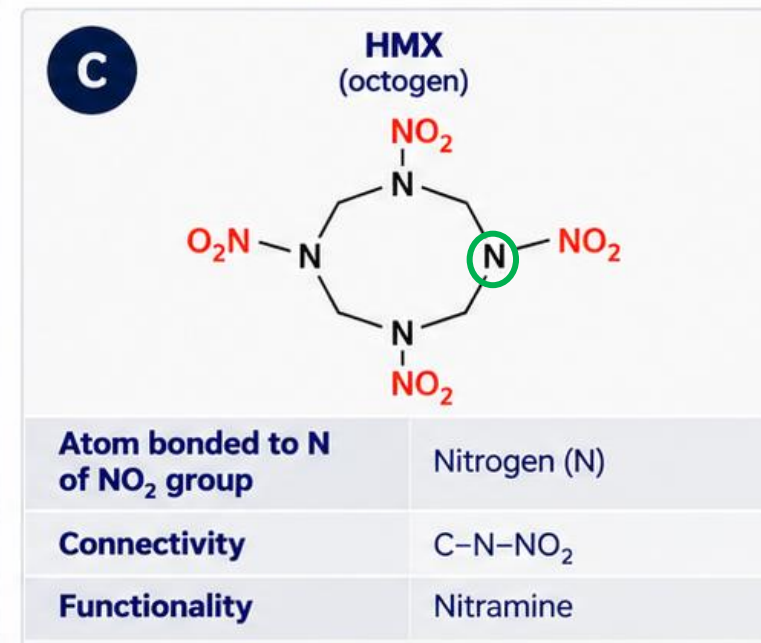
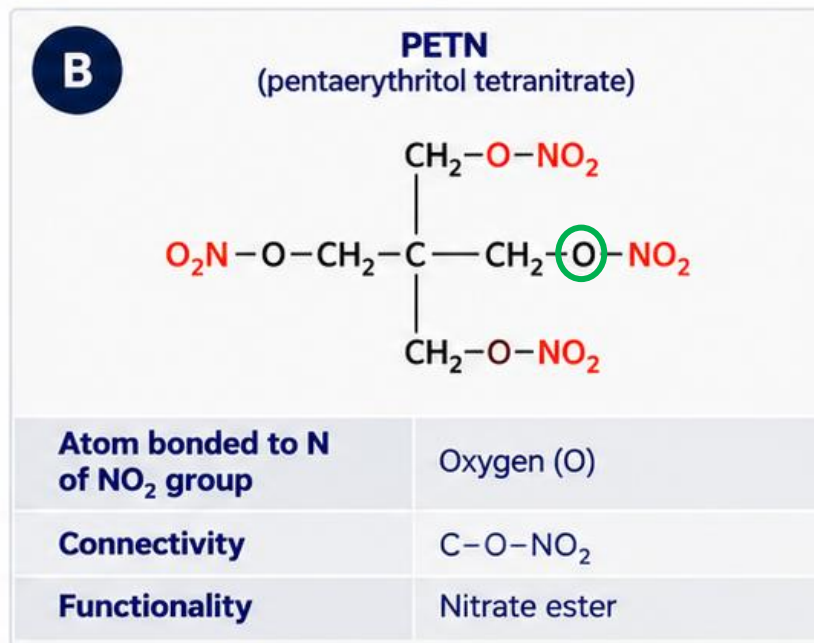
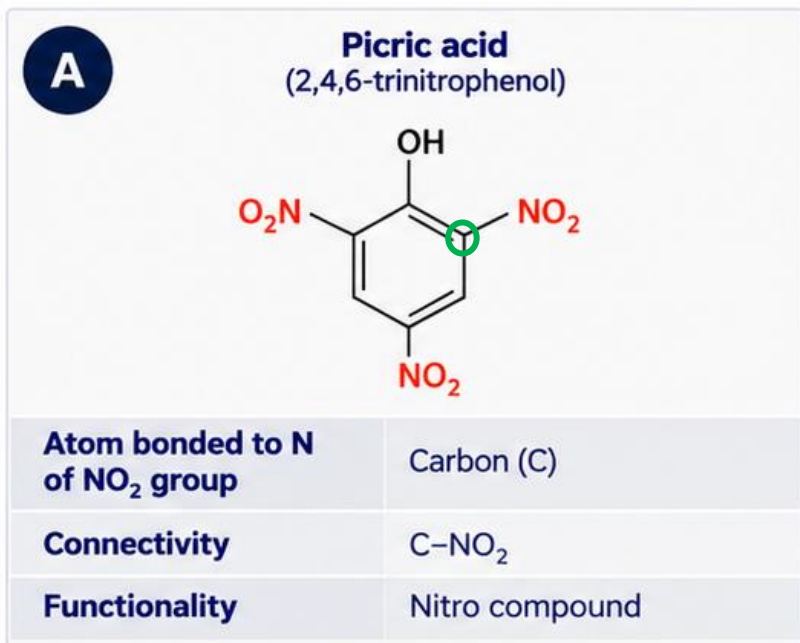


- 1 For each molecule, identify the atom directly bonded to the nitrogen of the NO₂ group and classify the energetic functionality.
- 2 Compare the local bonding environments of the NO₂-containing functionalities in A, B and C. What important differences can you identify?
- 3 Would you expect the NO₂ groups in these molecules to undergo the same chemistry? Justify your answer using connectivity and electronic environment.

Activity: same NO₂ unit, same chemistry? – Answers

Ch1

Each material contains nitrogen–oxygen functionality, but with different connectivity.



2

Comparison of local bonding environments

A: Picric acid

Nitrogen is bonded directly to an aromatic carbon (C–NO₂). The nitro group interacts with the aromatic π system.

B: PETN

Nitrogen is bonded to oxygen (C–O–NO₂), giving a nitrate ester environment.

C: HMX

Nitrogen is bonded to another nitrogen (C–N–NO₂), giving a nitramine environment.

3

Would you expect the NO₂ groups to undergo the same chemistry?

No.

Although all three materials contain NO₂ groups, the nitrogen is attached through different atoms (C, O or N). This gives different electronic environments and different reaction chemistry.

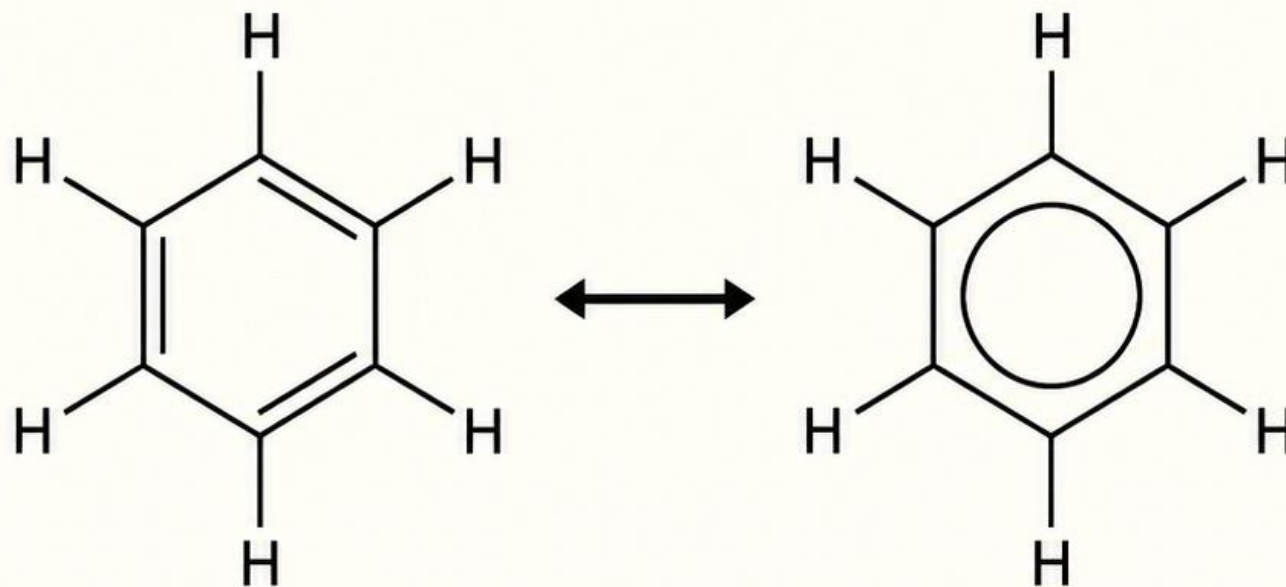
Key message:

Seeing –NO₂ is not enough. We must ask what it is bonded to.
Connectivity determines **functionality**, and functionality influences **chemistry**.

Benzene: an aromatic ring

Benzene, C_6H_6 , is a six-carbon ring with delocalised π electrons.

- Six carbon atoms in a ring.
- Each carbon is bonded to two other carbons and one hydrogen.
- The π electrons are delocalised over the whole ring, not simply three isolated double bonds.
- This delocalisation makes benzene particularly stable.



Key point:

Benzene tends to react in ways that preserve or restore its aromatic system.

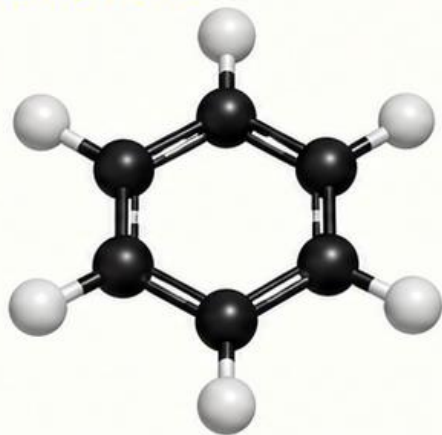


σ and π bonding in benzene

Each carbon atom in benzene is sp^2 hybridised.

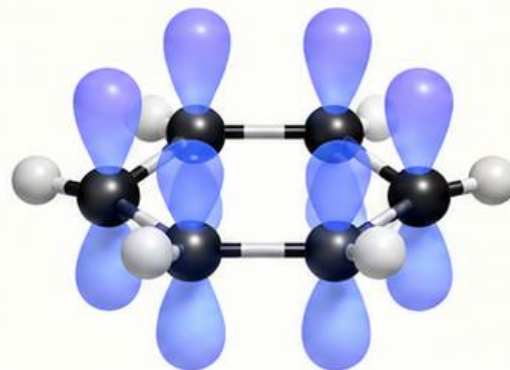
σ bonds: ring framework

- Each carbon forms three σ bonds in the plane of the ring.
- σ bonds are C–C and C–H.
- These σ bonds create a strong, planar ring framework.

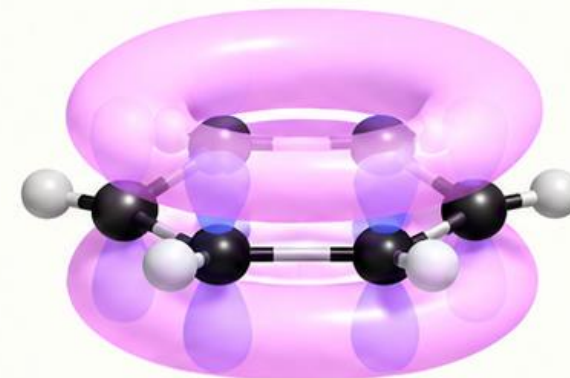


π system: delocalised electrons

- Each carbon has one unhybridised p orbital perpendicular to the ring.
- The six p orbitals overlap to form a delocalised π system above and below the ring.
- The π electrons are delocalised over the whole ring, not just between two carbons.



Six p orbitals (one on each carbon) overlap around the ring.



Delocalised π -electron system above and below the ring.

Key point:

The σ bonds form the ring framework, and the delocalised π system provides electron density above and below the ring, which is involved in the chemical reactivity of benzene.

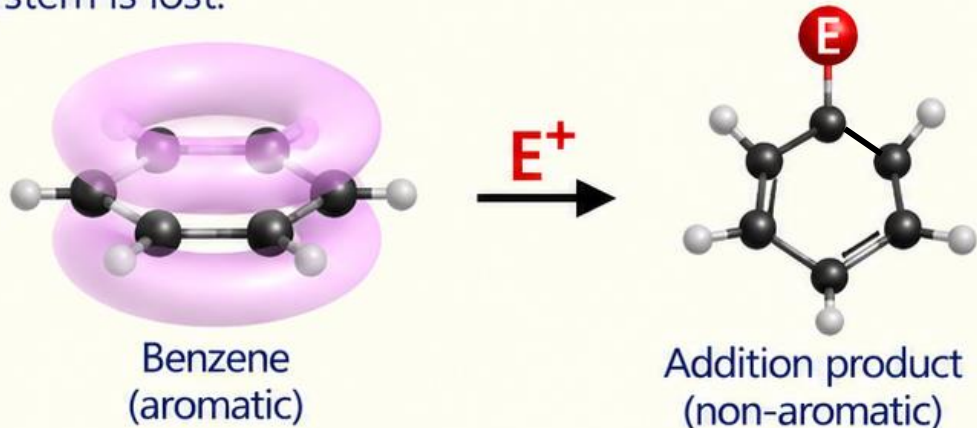


Why substitution rather than addition?

Benzene reacts with electrophiles in substitution reactions.

Addition

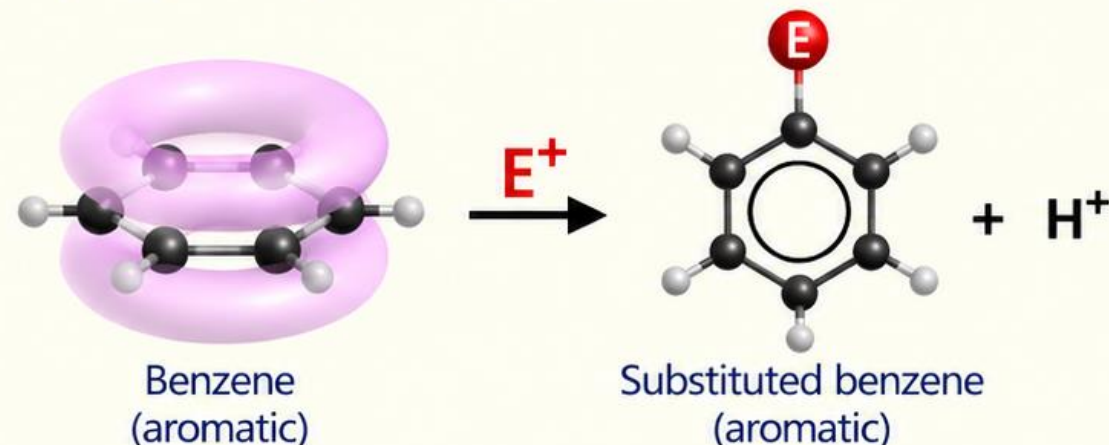
Electrophile adds to the ring and the aromatic system is lost.



- Electrophile reacts with the π system.
- Delocalisation of π electrons is disrupted.
- The final product is **not** aromatic.
- Aromatic stabilisation is lost, so addition is unfavourable for benzene.

Substitution

A hydrogen is replaced and the aromatic system is restored.



- Electrophile initially reacts with the π system.
- A hydrogen is removed as H^+ .
- The aromatic π system is **restored** in the final product.
- The substituted product is aromatic and therefore more stable.

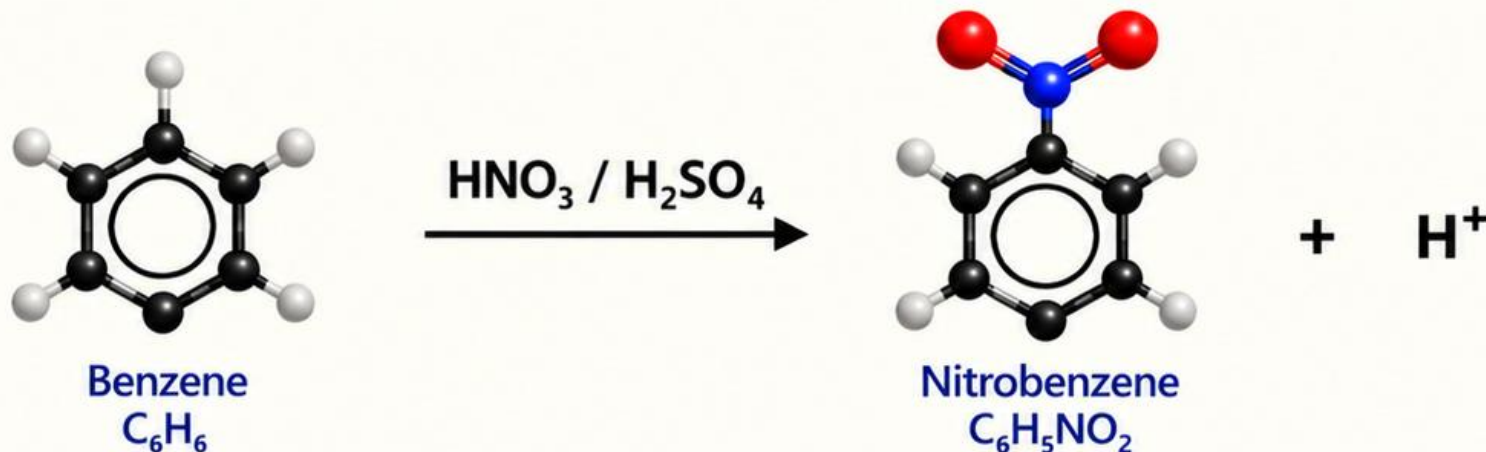
Key point:

Substitution is favoured because the delocalised aromatic π system is restored in the final product.



Nitration: introducing -NO_2 onto an aromatic ring

Benzene reacts with a strong electrophile in an electrophilic aromatic substitution.

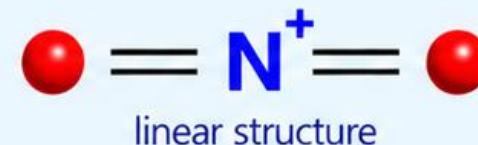


What changes?

- One C–H bond is replaced by a C– NO_2 bond.
- The aromatic ring is **retained** in the product.
- This is an electrophilic aromatic substitution.

Where does the -NO_2 group come from?

The electrophile that attacks the aromatic π system is the **nitronium ion**, NO_2^+ .



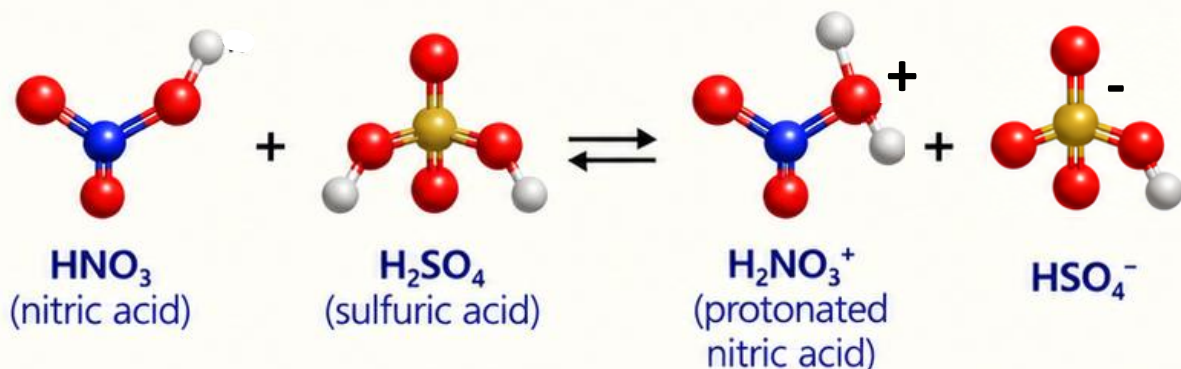
Key point:

Nitration requires an electrophile strong enough to react with the electron-rich aromatic π system.

How is the nitronium ion formed?

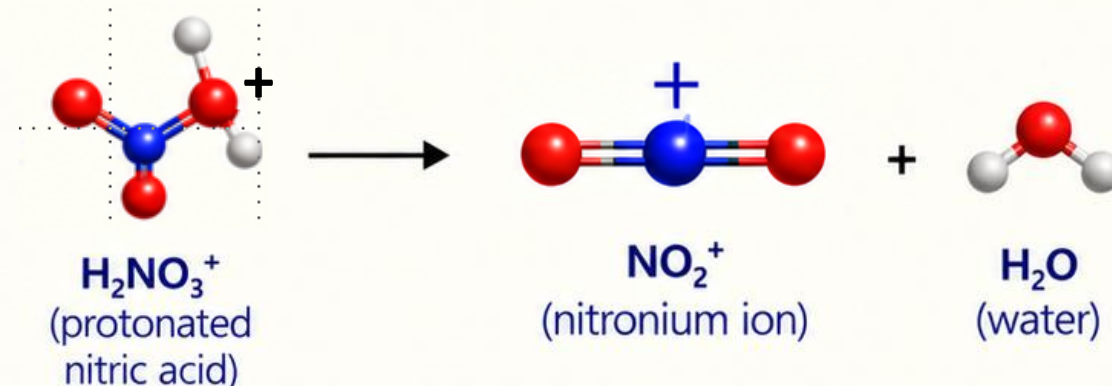
Nitric acid is activated by sulfuric acid to generate NO_2^+ .

1 Protonation of nitric acid



- H_2SO_4 is the stronger acid and donates a proton (H^+).
- HNO_3 accepts H^+ to form H_2NO_3^+ .
- Protonation converts an $-\text{OH}$ group into a much better leaving group (H_2O).

2 Loss of water



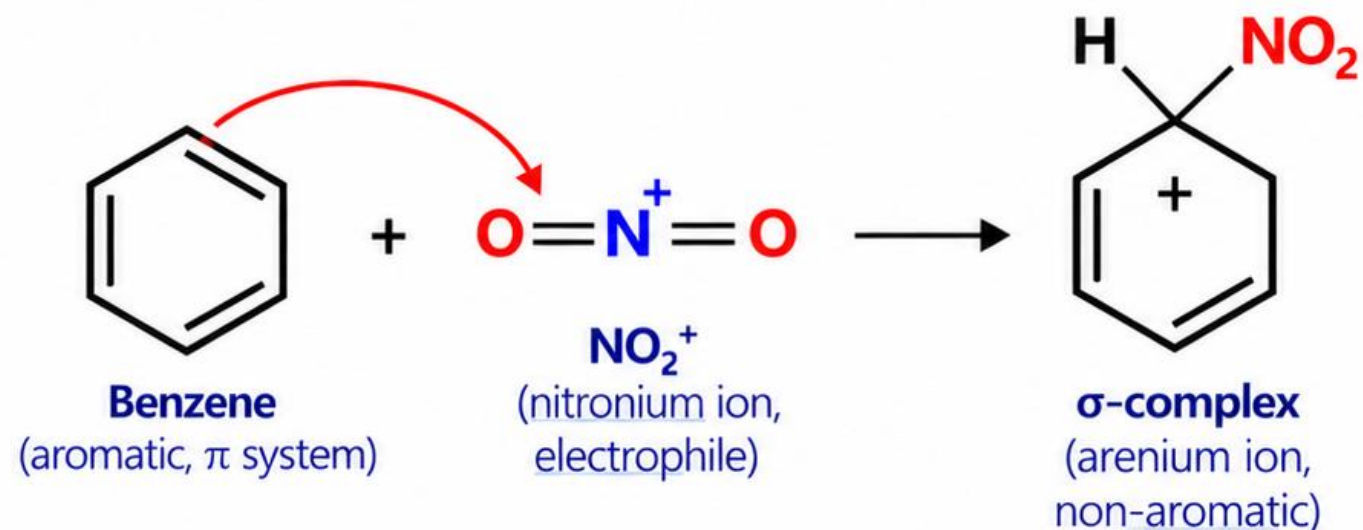
- The protonated nitric acid loses a molecule of water.
- This generates the nitronium ion, NO_2^+ .
- NO_2^+ is a strong electrophile that can react with the electron-rich aromatic π system.

Key point:

The nitrating mixture (HNO_3 / H_2SO_4) generates the nitronium ion, NO_2^+ , which is the electrophile in aromatic nitration.

Step 1: electrophilic attack by NO_2^+

A pair of π electrons from benzene reacts with the nitronium ion to form a σ -complex.



Curved arrow notation



A curved arrow shows the movement of a pair of electrons,
not the movement of an atom.

What has happened?

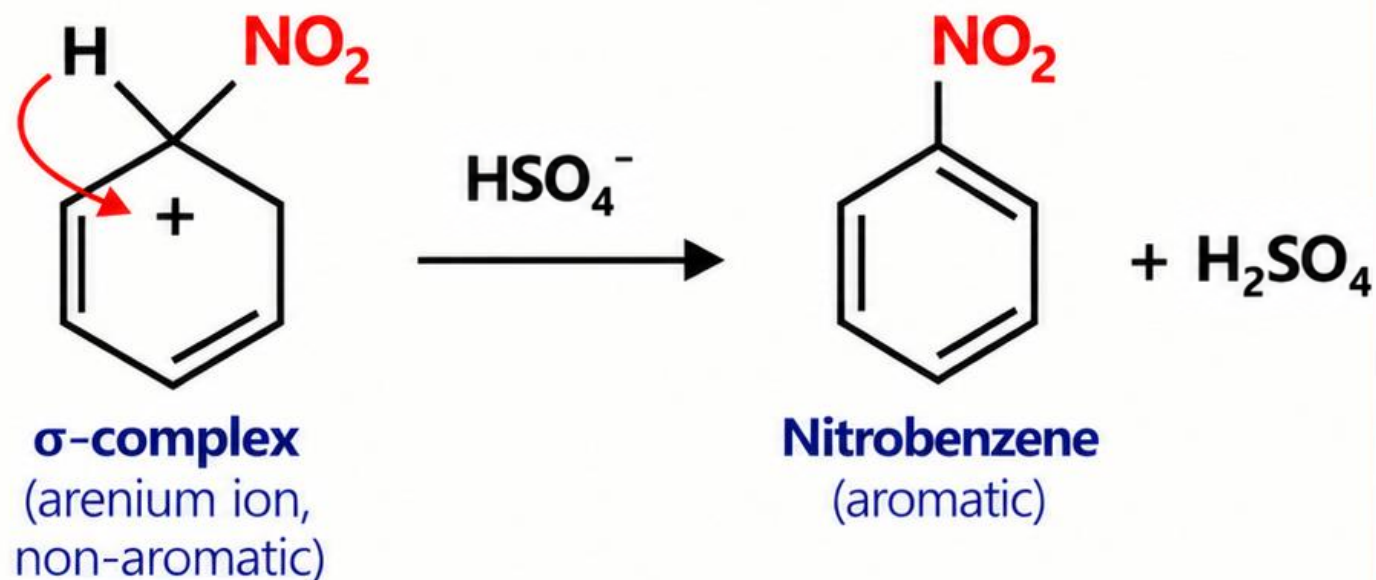
- A pair of π electrons from benzene forms a new C–N bond with NO_2^+ .
- NO_2^+ has been added to one carbon of the ring.
- The carbon now has both H and NO_2 attached.
- The continuous aromatic π system is temporarily disrupted.
- The intermediate carries a positive charge delocalised over the ring.

Key point: The electrophilic attack forms the C– NO_2 bond, but temporarily sacrifices aromaticity.



Step 2: restoration of aromaticity

A base removes H^+ from the σ -complex, reforming the aromatic π system.



What has happened?

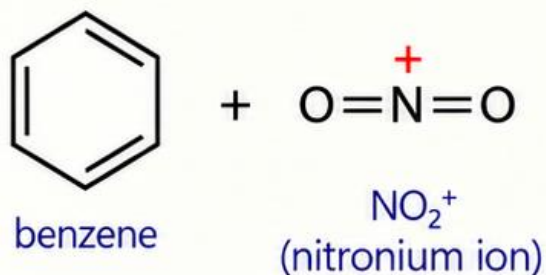
- HSO_4^- removes a proton (H^+) from the carbon that bears NO_2 .
- The electrons from the C-H bond reform a π bond in the ring.
- The aromatic π system is restored.
- Nitrobenzene is formed.
- Sulfuric acid is regenerated.

Key point: Removal of H^+ restores the aromatic π system, giving a stable aromatic product (nitrobenzene).

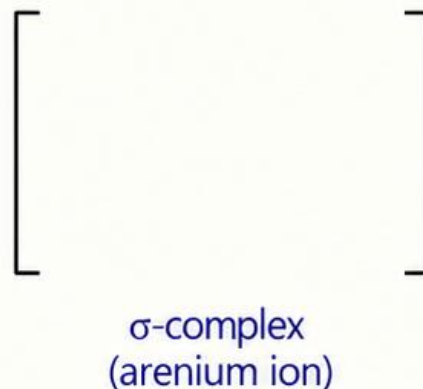
Activity: can you complete the mechanism?

Add the missing curved arrows and draw the σ -complex intermediate.

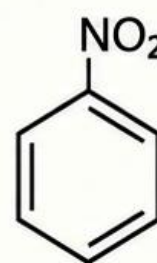
1. Attack by electrophile



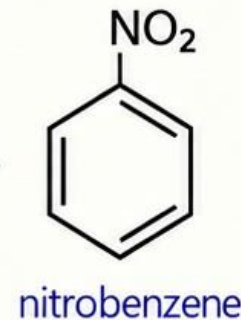
2. σ -Complex formation (draw the intermediate)



3. Deprotonation



4. Product and by-product



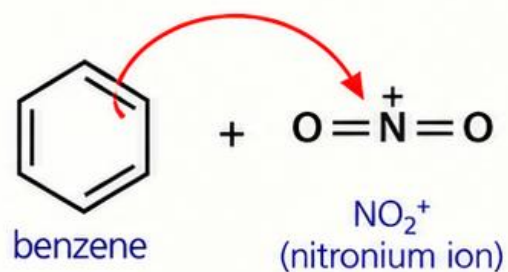
- 1 Add the missing curved arrows for each step of the mechanism.
- 2 Draw the σ -complex intermediate, with NO₂ and H on the same carbon of the ring. Show the positive charge and any relevant resonance structure(s).
- 3 Explain what happens to the aromaticity of the ring during the reaction and at which step it is lost and restored.
- 4 Identify the electrophile in this reaction and explain (a) why it is electrophilic and (b) why loss of H⁺ gives substitution rather than retention of the addition product.



Activity solution: electrophilic aromatic nitration

Completed mechanism with curved arrows and σ -complex intermediate.

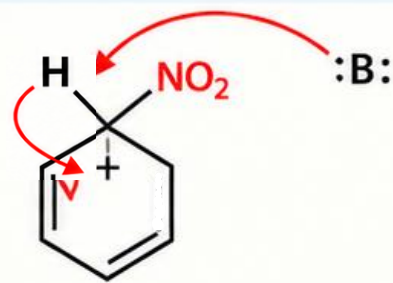
1. Attack by electrophile



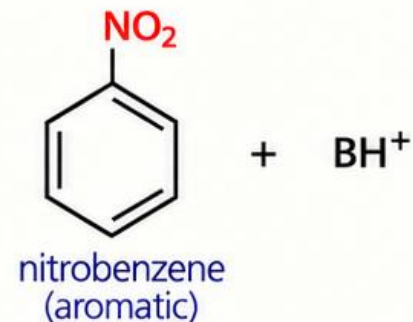
2. σ -Complex formation (arenium ion)



3. Deprotonation



4. Product and by-product



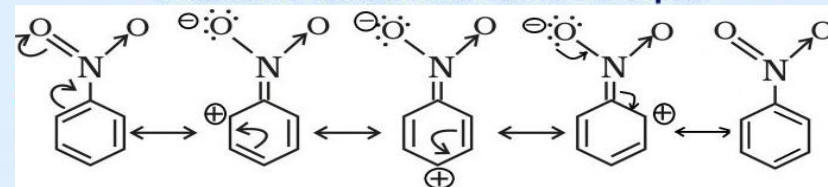
1 Curved arrows for each step

- **Step 1:** a curved arrow from the aromatic π bond to the nitrogen atom of NO_2^+ .
- **Step 3:** one curved arrow from the C–H bond to the ring to reform the π bond and one curved arrow from the C–H bond to the base (B:).

2 σ -Complex intermediate

- H and NO_2 are on the same carbon of the ring.
- The carbon is sp^3 hybridised and the ring is non-aromatic.
- The positive charge is delocalised over three ring carbons (draw all three resonance contributors, as shown below).

Resonance contributors of the σ -complex



3 Aromaticity during the reaction

- Aromaticity is lost after the electrophilic attack, when the σ -complex is formed (the ring is no longer fully conjugated).
- Aromaticity is restored after deprotonation, when a π bond is re-formed and nitrobenzene (aromatic) is produced.

4 Electrophile and why substitution occurs

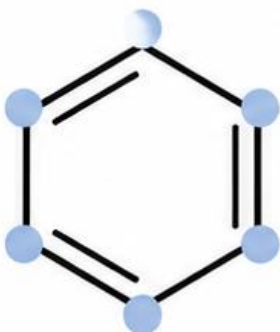
- The electrophile is the nitronium ion, NO_2^+ .
- It is electrophilic because nitrogen carries a positive charge and is electron-deficient.
- Loss of H^+ restores the aromatic π system, giving an aromatic product. Retaining the addition product would leave the ring non-aromatic and is therefore much less favourable.

A substituent changes the next reaction

Once a group is attached to the ring, the carbon atoms are no longer equivalent.

1 Benzene: all positions are equivalent

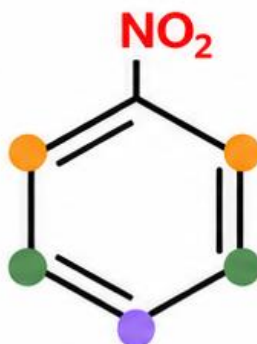
All six carbon atoms in benzene are electronically equivalent.



- Each carbon has the same electron density.
- Electrophilic attack can occur at any position with the same probability.
- Only one monosubstituted product is formed.

2 After substitution: positions are no longer equivalent

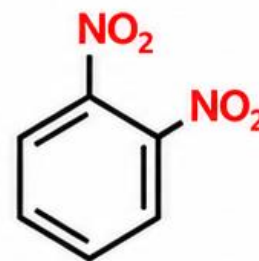
When a group is attached, it affects the electron density in the ring.



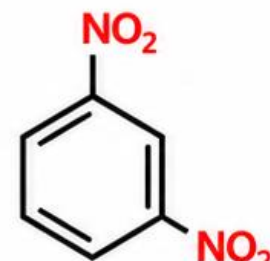
- Ortho positions (2 and 6)
– next to the substituent
- Meta positions (3 and 5)
– separated by one carbon
- Para position (4)
– opposite the substituent

3 Three possible positions for the next substitution

A second electrophile can attack at an ortho, meta or para position, giving different products.



Ortho product
(2-substitution)



Meta product
(3-substitution)



Para product
(4-substitution)

Key point: The group already attached to an aromatic ring changes both its reactivity and the position of subsequent substitution.

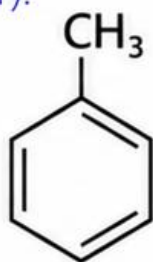
Two questions: how fast and where?

When a substituent is already on the ring, we need to consider two different questions in electrophilic aromatic substitution.

1. How fast?

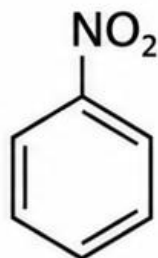
Reactivity

- How quickly does the ring react with an electrophile?
- Some substituents make the ring more reactive (faster).
- Others make the ring less reactive (slower).



faster

activating substituent



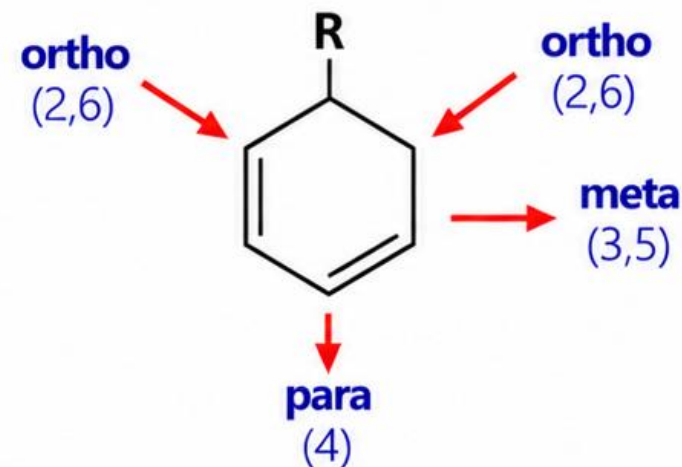
slower

deactivating substituent

2. Where?

Regioselectivity

- At which position on the ring does the electrophile attack?
- The substituent directs the incoming group to particular positions: ortho, meta or para.



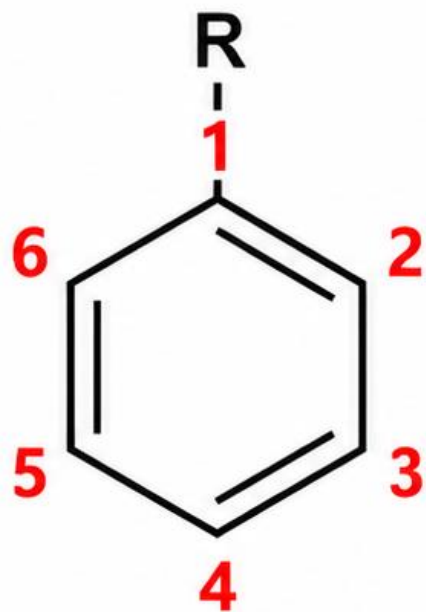
Key point:

A substituent can affect both the rate of reaction (how fast) and the position of substitution (where).

Ortho, meta and para positions

Positions on the aromatic ring are named relative to the existing substituent.

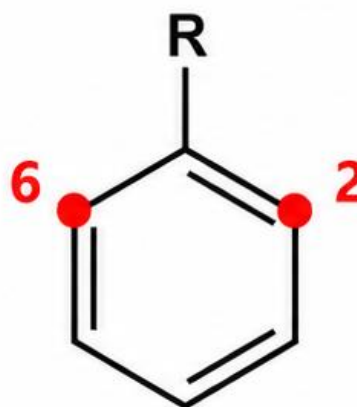
Numbering the ring



Relative positions

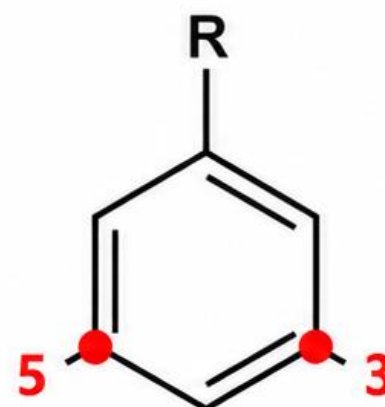
ortho

(2- and 6-positions)



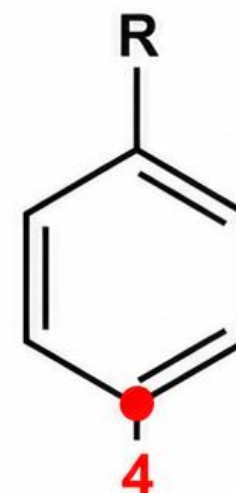
meta

(3- and 5-positions)



para

(4-position)



Key point:

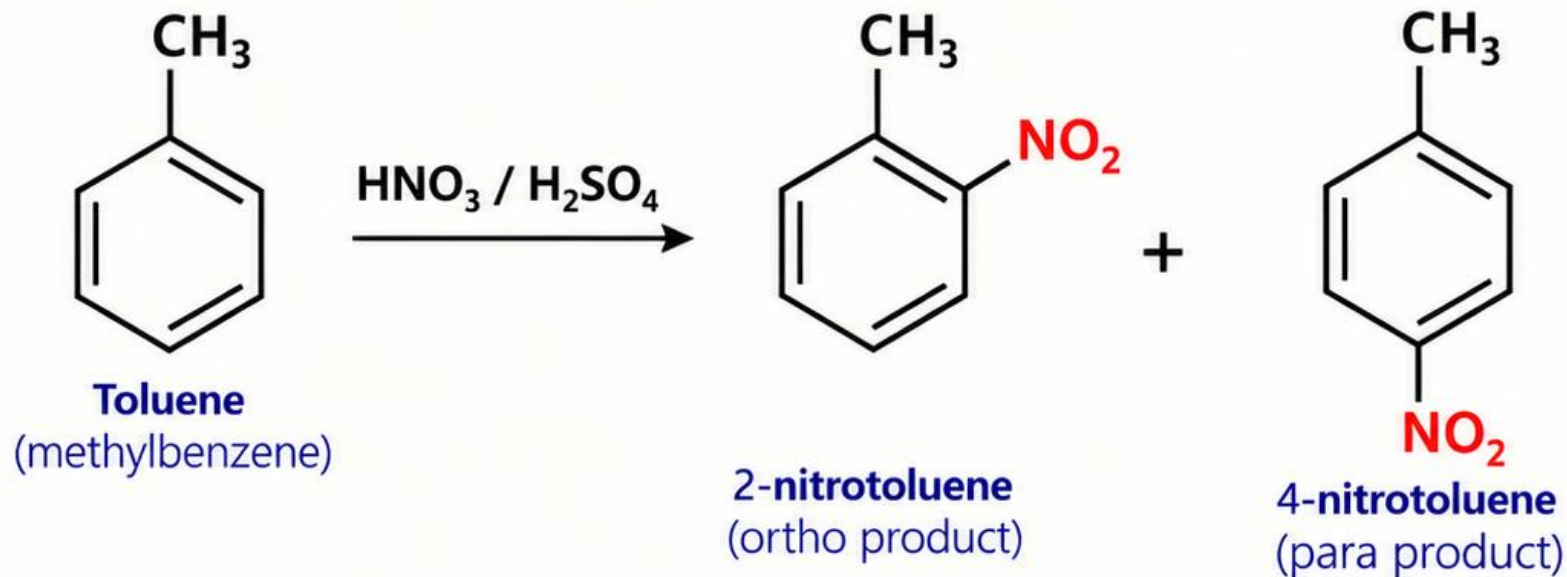
Ortho, meta and para describe the position of a new substituent relative to an existing group on the aromatic ring.

The CH₃ group: electron donating, activating, ortho/para directing

Ch3

The methyl group increases electron density in the aromatic ring.

- The CH₃ group donates electron density to the ring through **inductive effect (+I)** and **hyperconjugation**.
- This increases the electron density in the aromatic ring.
- The ring is more **reactive** towards electrophilic **substitution** (**activating group**).
- The next substitution is favoured at the **ortho** and **para** positions (**ortho/para directing group**).



Key point:

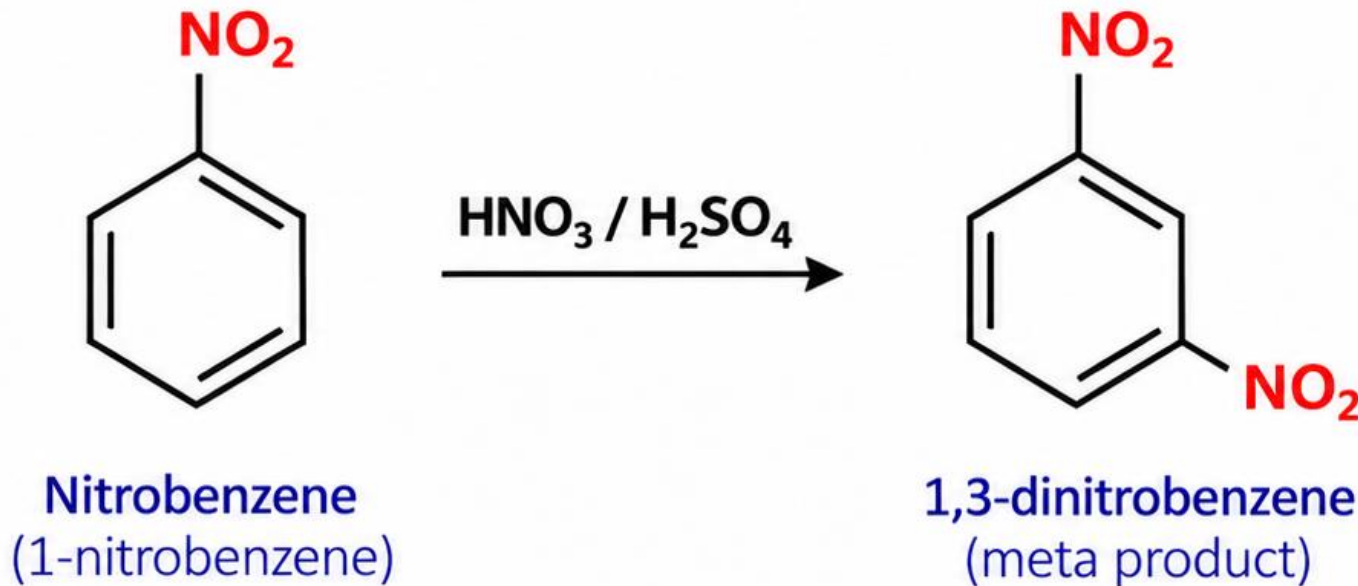
The CH₃ group donates electron density to the aromatic ring, making it more reactive and directing the next substitution to the **ortho** and **para** positions.



The -NO_2 group: electron withdrawing, deactivating, meta directing Ch3

The nitro group withdraws electron density from the aromatic ring.

- The -NO_2 group strongly withdraws electron density from the ring through the **inductive effect ($-\text{I}$)** and **resonance ($-\text{M}$)**.
- This makes the ring less reactive towards electrophilic substitution (**deactivating**).
- Ortho and para positions are electron-deficient.
- The next substitution is favoured at the **meta** position (**meta directing**).

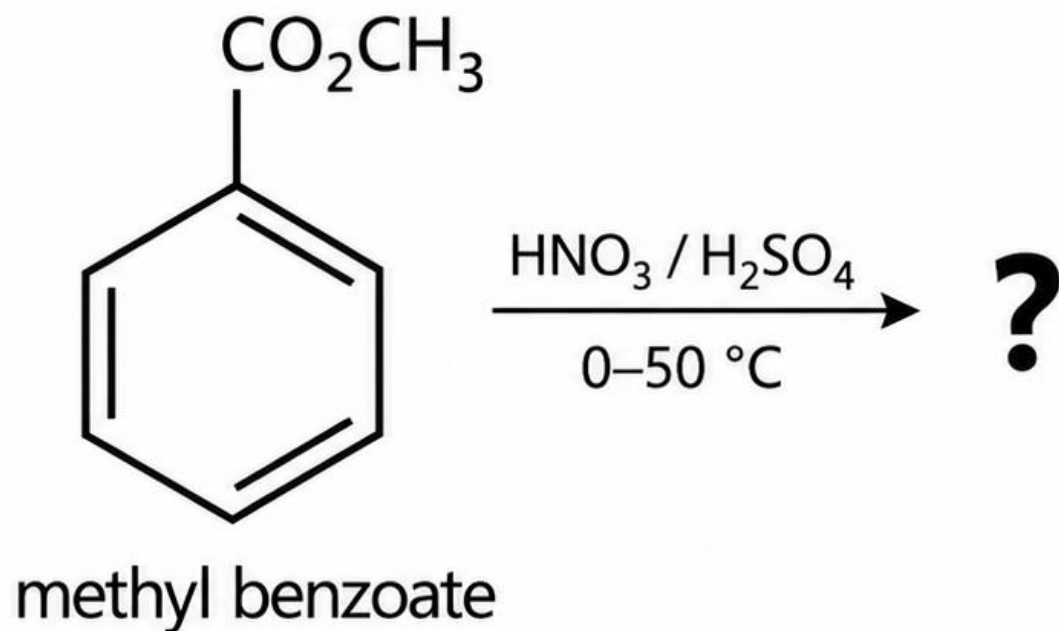


Key point:

The -NO_2 group withdraws electron density, making the ring less reactive towards electrophilic substitution and directing the next substitution to the **meta** position.



Use what you have learned about substituent effects to make a prediction.



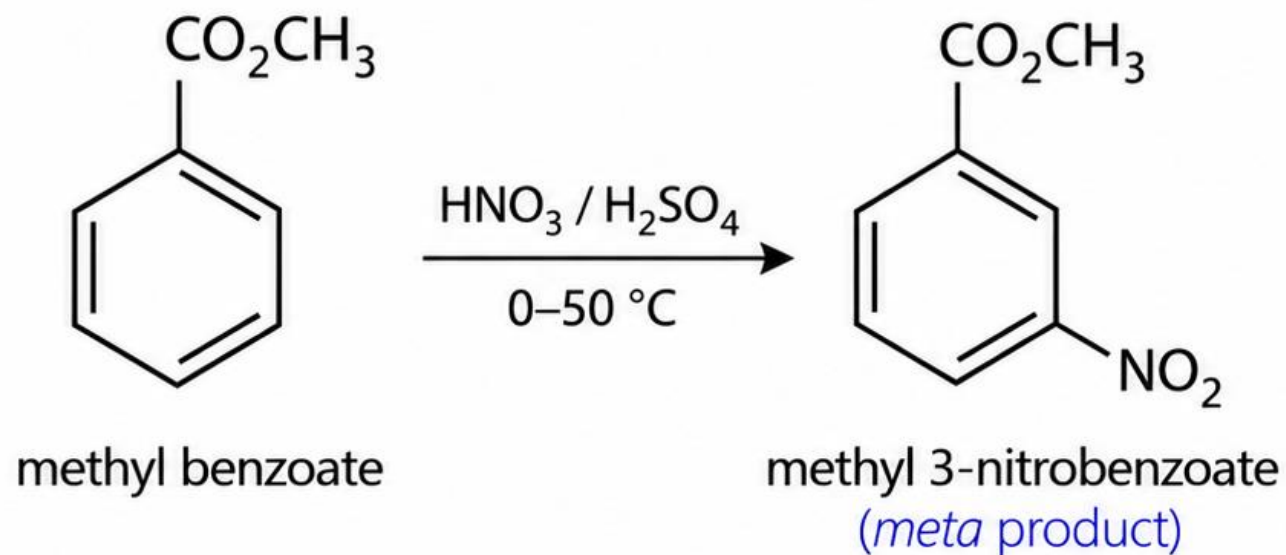
- 1 Is $-\text{CO}_2\text{CH}_3$ electron donating or electron withdrawing?
- 2 Would $-\text{CO}_2\text{CH}_3$ activate or deactivate the aromatic ring towards EAS?
- 3 Which position should be favoured for nitration — *ortho*, *meta* or *para*? Justify your prediction using σ -complex stability.

Cranfield connection:

You will investigate this nitration experimentally at **Cranfield**.

Activity solution: nitration of methyl benzoate

Ch3



1

$-\text{CO}_2\text{CH}_3$ is **electron withdrawing** ($-I$ and $-M$).

2

It **deactivates** the aromatic ring towards electrophilic substitution.

3

Meta attack is favoured because it avoids the particularly destabilised σ -complex contributor with the positive charge on the carbon bearing $-\text{CO}_2\text{CH}_3$.

Key point:

Electron withdrawal explains both **lower reactivity** and **meta direction**, but through related rather than identical effects.

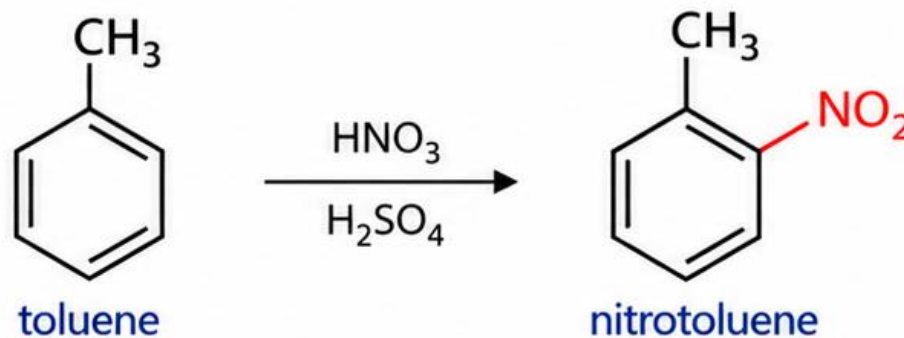
Cranfield connection:

Prediction $\rightarrow$ experiment $\rightarrow$ product identification.



Successive substitution changes the next reaction

Each nitration changes the substituents on the ring and therefore the reactivity and regioselectivity of the next nitration.



The product of the first reaction is the starting material for the second.

CH_3 group

- activating (increases electron density)
- ortho/para directing
- makes the ring more reactive

NO_2 group

- deactivating (withdraws electron density)
- meta directing
- makes the ring less reactive

Where will the next NO_2 group enter when both substituents influence the ring?

Key point:

Successive substitution is not simply repetition of the same reaction: every new substituent changes the reactivity and regioselectivity of the ring.

Where will the next nitration occur?

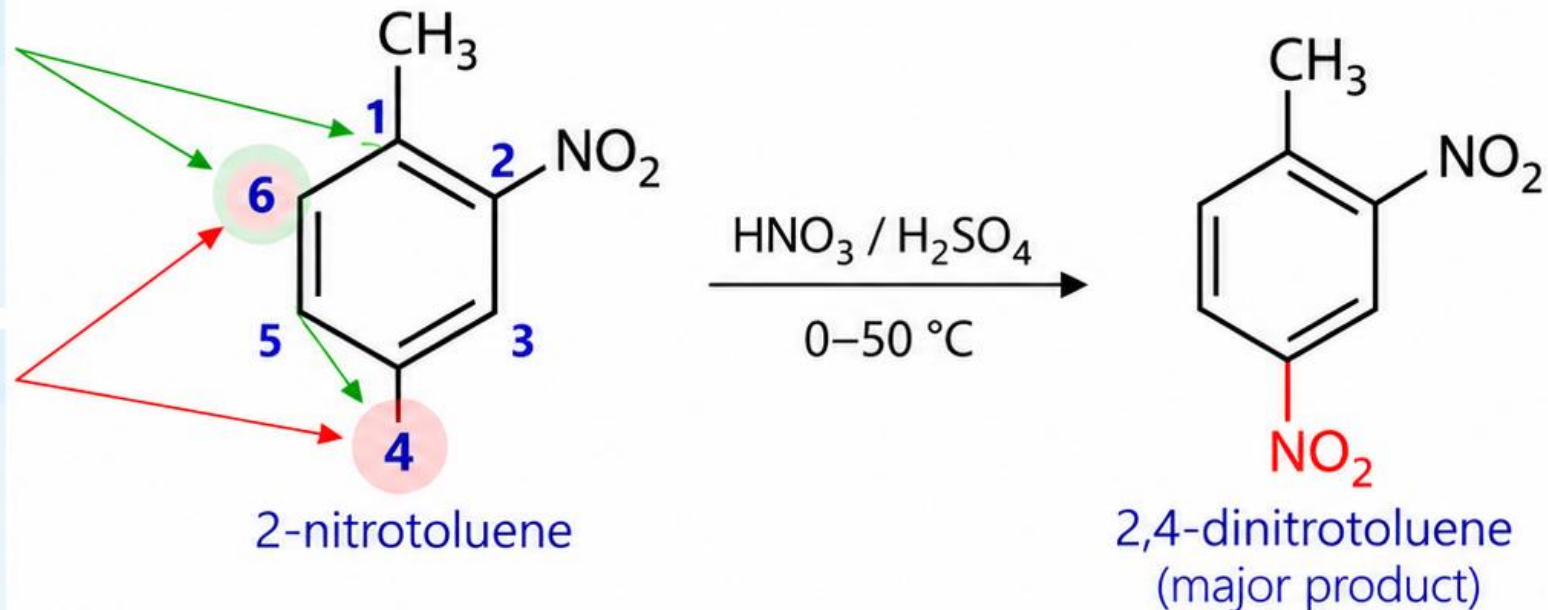
Consider the directing effects of both substituents and any steric effects.

Effect of CH₃ group (at C1)

- Activating (increases electron density)
- Ortho/para directing
- Favours positions 2, 4 and 6

Effect of NO₂ group (at C2)

- Deactivating (withdraws electron density)
- Meta directing (relative to NO₂)
- Favours positions 4 and 6



- Both substituents direct the next NO₂ group to **positions 4 and 6**.
- Position 6 is **sterically hindered** between CH₃ and NO₂, so **position 4 is favoured**.
- The major product is **2,4-dinitrotoluene** (nitration at position 4).

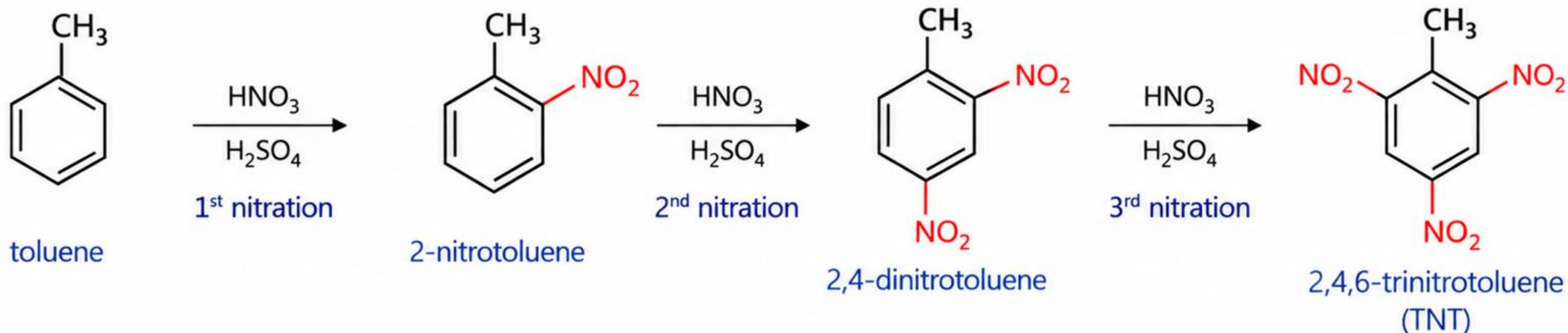
Key point:

When more than one substituent is present, consider the directing effects of **all substituents together** and any **steric effects** to determine the most likely position.



Sequential nitration: from toluene towards TNT

Each nitration changes the substrate for the next reaction.



- The CH_3 group activates the ring and directs ortho/para.
- Each added NO_2 group deactivates the ring, so successive nitrations become more difficult.

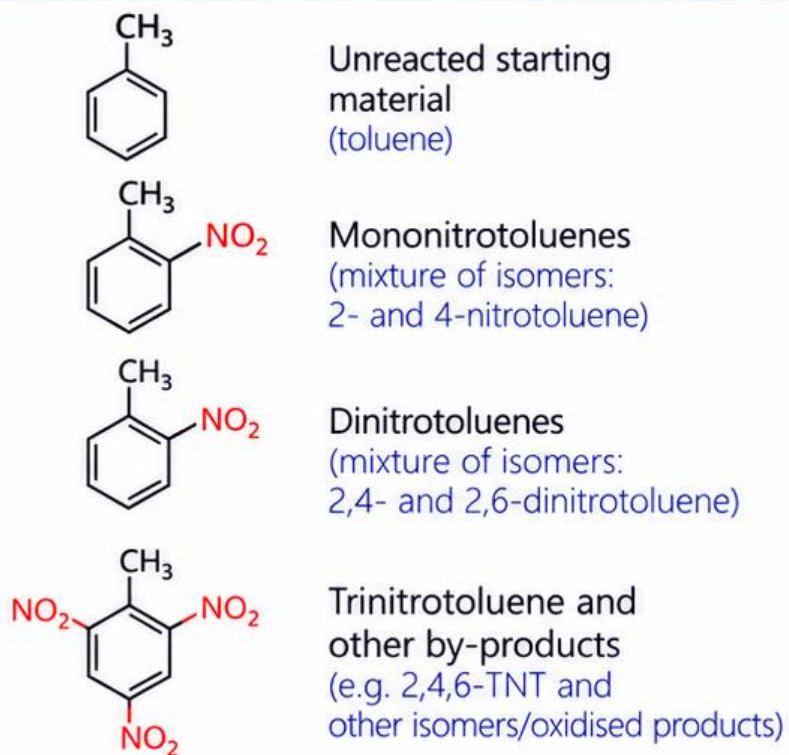
Key point:

Sequential nitration changes both the regioselectivity and the reactivity of the ring at every stage.

What leaves manufacture?

The nitration of toluene produces a mixture, not a single pure product.

1. Reaction mixture

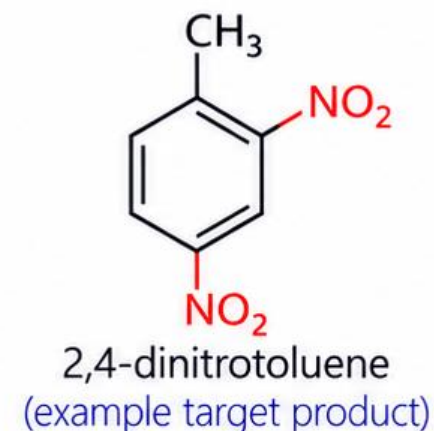


2. Separation / purification

The reaction mixture is separated to isolate the desired product(s).

- remove unreacted toluene
- separate different isomers (e.g. by distillation, crystallisation, chromatography)
- remove by-products and impurities
- obtain the target compound in purified form

3. Characterised material



- identity (which compound)
- purity (how much target product)
- composition (what else is present)
- suitable for next processing step

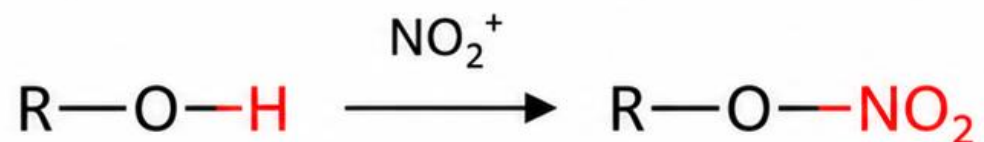
Key point:

Nitration gives a mixture of products. A single pure compound must be isolated and characterised before it can leave the manufacturing stage.

O-nitration: forming nitrate esters

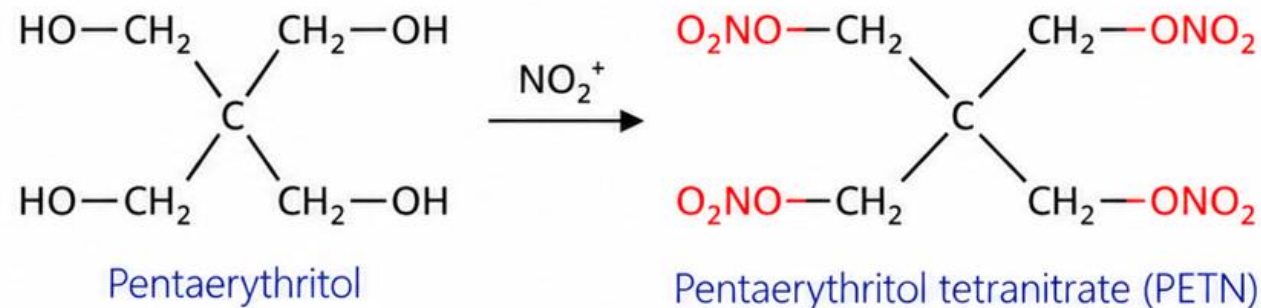
Nitration at oxygen converts an alcohol into a nitrate ester.

General reaction

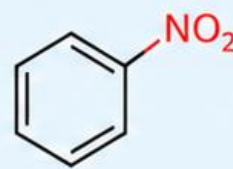


- Nitration occurs at oxygen, not at carbon.
- The original C–O bond is retained.
- The product contains the characteristic C–O–NO₂ nitrate ester connectivity.

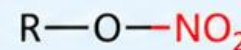
Example: pentaerythritol to PETN



Comparison of connectivity



Nitro compound
C–NO₂
(no oxygen)



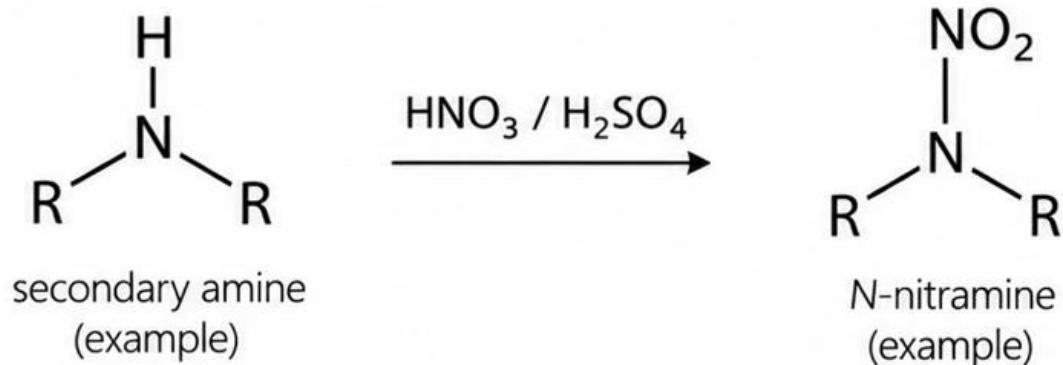
Nitrate ester
C–O–NO₂
(oxygen between C and NO₂)

Key point:

O-nitration converts an alcohol into a nitrate ester: the oxygen of the original –OH group becomes part of the C–O–NO₂ linkage.

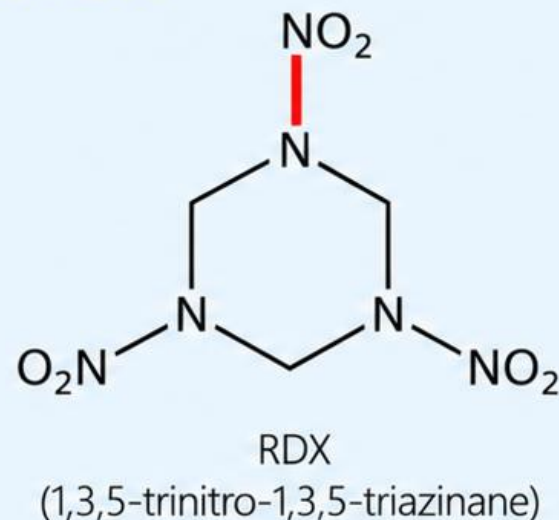
N-nitration: forming nitramines

A nitrogen atom (N–H) reacts to give an N–NO₂ bond.



- N-nitration replaces a hydrogen on nitrogen (N–H) with a nitro group to form an N–NO₂ bond.
- The nitrogen atom of the starting material becomes directly bonded to the nitrogen of the nitro group.
- The product is a nitramine.

Example: RDX



Question:

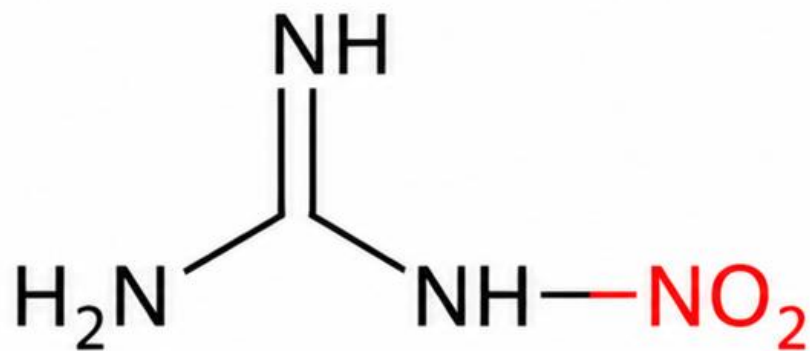
Which bond tells you this is a nitramine rather than a nitro compound or nitrate ester?

Key point:

N-nitration introduces an N–NO₂ bond (C–N–NO₂) to give nitramine functionality, which is chemically distinct from nitrate esters (C–O–NO₂) and nitro compounds (C–NO₂).

Applying connectivity: nitroguanidine

Use the structure to identify the nitration pathway and the energetic functionality.



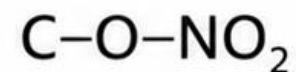
Nitroguanidine

Where is the NO₂ group actually attached?

Choose the correct energetic functionality based on connectivity.



nitro compound



nitrate ester



nitramine

Correct option:

C–N–NO₂ (nitramine)

Nitration pathway:

N-nitration (at nitrogen)

Reason:

The NO₂ group is bonded to nitrogen (C–N–NO₂ connectivity), not directly to carbon and not through oxygen.

Key point:

Identify the nitration pathway from the connectivity, not just the presence of NO₂.

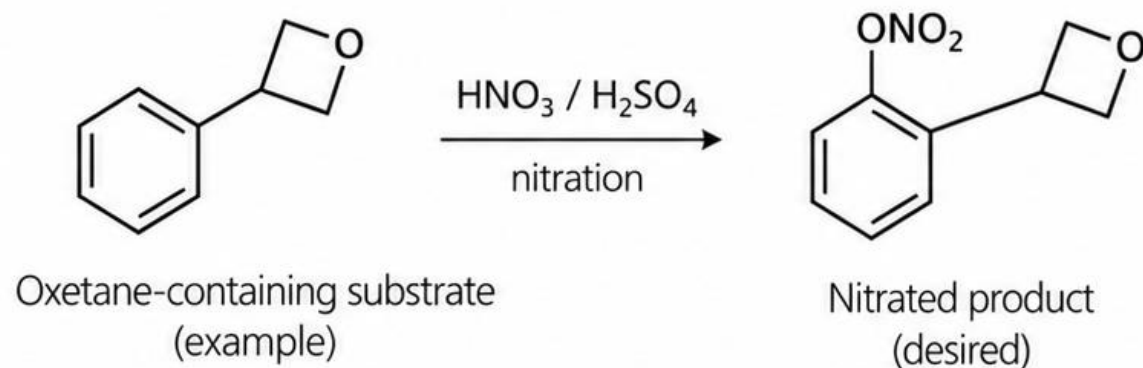


When nitration affects more than the intended site

Strongly acidic nitration conditions can also change the molecular framework.

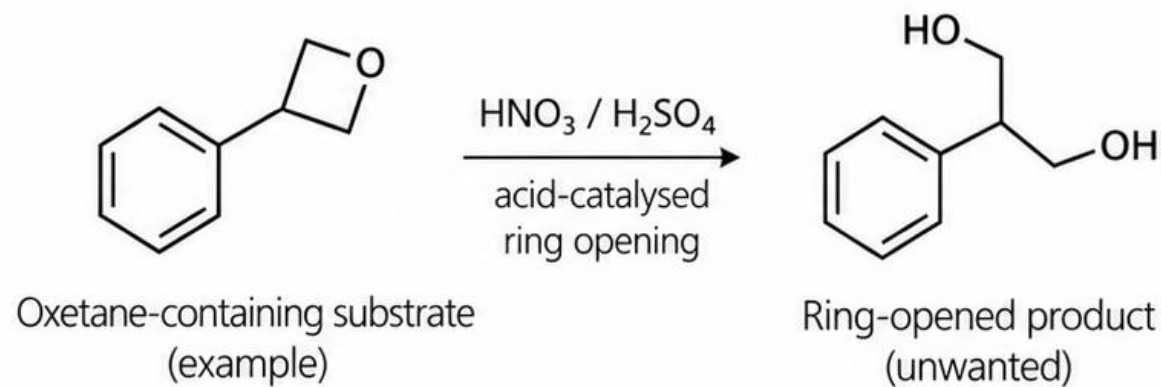
Intended chemistry

Introduce the required nitrate functionality.



Competing chemistry

Strongly acidic conditions can also cause oxetane ring opening.



Question:

If the desired nitration occurs but the molecular framework is also altered, has the reaction been successful?

The research challenge:

reaction
conditions



selectivity



functional-group
compatibility



product
integrity

From reaction chemistry to the laboratory

Mechanistic chemistry generates hypotheses. Experimental chemistry establishes what actually formed.

What chemistry allows us to predict

From structure and mechanism we can predict:

- likely reaction pathway
- likely reactive site
- possible products and isomers
- possible competing reactions
(e.g. side reactions, decomposition,
unwanted functional-group reactions)

PREDICTION



EXPERIMENT

EVIDENCE

What experiment must establish

Experimental evidence tells us:

- what was actually formed
- identity of products
(target material, isomers, by-products)
- product distribution
- conversion and yield
- purity
(presence of unreacted starting material
and other impurities)

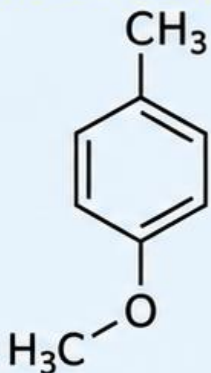
Question:

What evidence would you need before claiming that the intended material had been successfully produced?

Can you follow the chemistry from structure to product?

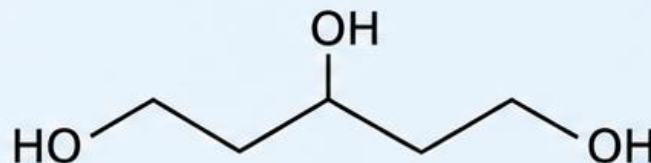
For each starting material, use your knowledge of molecular structure, reactivity and nitration to make a chemical prediction.

A. Substituted aromatic compound



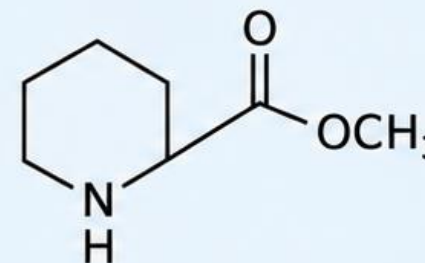
1-methoxy-4-methylbenzene
(*p*-methylanisole)

B. Multifunctional alcohol



pentane-1,3,5-triol
(three hydroxyl groups)

C. Nitrogen-containing compound with another reactive functionality



methyl piperidine-2-carboxylate
(secondary amine and ester)

- 1 Predict** the most likely nitration pathway and product connectivity (C–NO₂, C–O–NO₂ or C–N–NO₂).
- 2 Justify** your prediction using molecular structure and electronic effects.
- 3 Identify** a plausible alternative product or competing reaction.
- 4 State** what experimental evidence you would need to test your prediction.

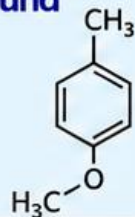
Key point:

Do not just identify where NO₂ could appear. Build and justify a chemical prediction.

Activity solution – from structure to product

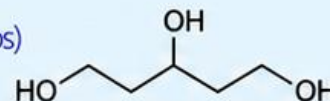
A. Substituted aromatic compound

1-methoxy-4-methylbenzene
(p-methylanisole)



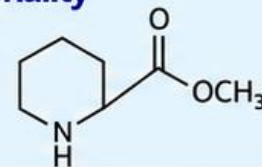
B. Multifunctional alcohol

pentane-1,3,5-triol
(three hydroxyl groups)



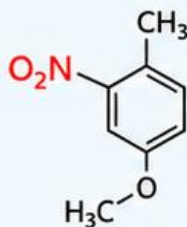
C. Nitrogen-containing compound with another reactive functionality

methyl piperidine-2-carboxylate
(secondary amine and ester)



1 Predicted nitration pathway and product(s)

C–NO₂ (aromatic nitration)



2-nitro-1-methoxy-4-methylbenzene
(major product, ortho to –OCH₃)

2 Why?

- OCH₃ is a strong activating, ortho/para-directing group.
- Para position is occupied by –CH₃, so nitration is favoured at the ortho positions (2 or 6, equivalent).

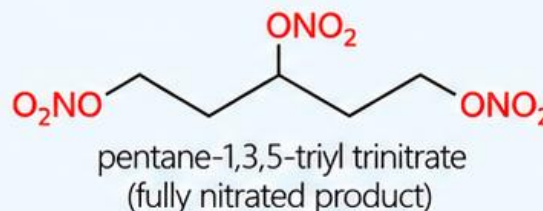
3 Other possible products

- Other regioisomer(s) (minor amounts) due to competing directing effects of –OCH₃ and –CH₃.

4 Experimental evidence needed

- Confirm product identity (e.g. NMR, IR, MS).
- Determine regioisomer distribution and purity (e.g. HPLC, GC).

C–O–NO₂ (nitrate esters)

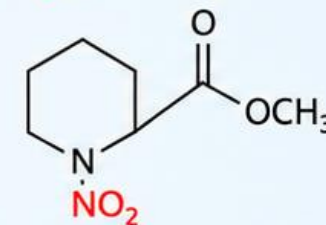


- Three –OH groups react to form nitrate ester (C–O–NO₂) linkages.
- Alcohol oxygens are nucleophilic and are converted to –ONO₂ under nitrating conditions.

- Partially nitrated products (mono- or di-nitrates) if not all three –OH groups react (incomplete conversion).

- Confirm degree of nitration (mono/di/tri).
- Establish identity and purity (e.g. NMR, IR, MS, elemental analysis).

C–N–NO₂ (nitramine)



- Secondary amine (N–H) provides a site for N-nitration to give a nitramine (C–N–NO₂).
- The ester group is less nucleophilic and is generally retained under these conditions.

- Competing reactions (e.g. O-nitration of the ester or protonation/decomposition) or alteration of the ring under strongly acidic conditions.

- Confirm N-nitration has occurred.
- Verify the ester and ring remain intact.
- Assess purity (e.g. NMR, IR, MS, HPLC).

Key point:

The starting structure tells us what chemistry is plausible; experimental evidence is needed to confirm what has actually been formed and to establish selectivity, composition and purity.



What have we learned?

We can use molecular structure to predict nitration chemistry, but experimental evidence is needed to establish what was actually formed.

1

Read the structure

Identify functional groups, connectivity and potential reactive sites.

2

Predict the chemistry

Use mechanism and electronic effects to predict reaction pathway and selectivity.

3

Consider what else could form

Account for isomers, incomplete reaction and competing chemistry.

4

Test the prediction

Use experimental evidence to establish identity, composition and purity.

Molecular
structure



Reaction
chemistry



Predicted
products



Experimental
evidence

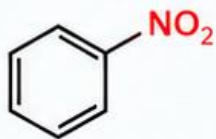


Manufactured
material

Different connectivity gives different classes of nitration products



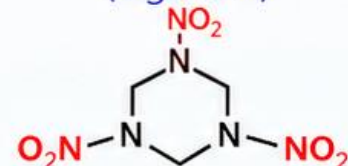
nitro compounds
(e.g. nitrobenzene)



nitrate esters
(e.g. nitroglycerin)



nitramines
(e.g. RDX)



Key point:

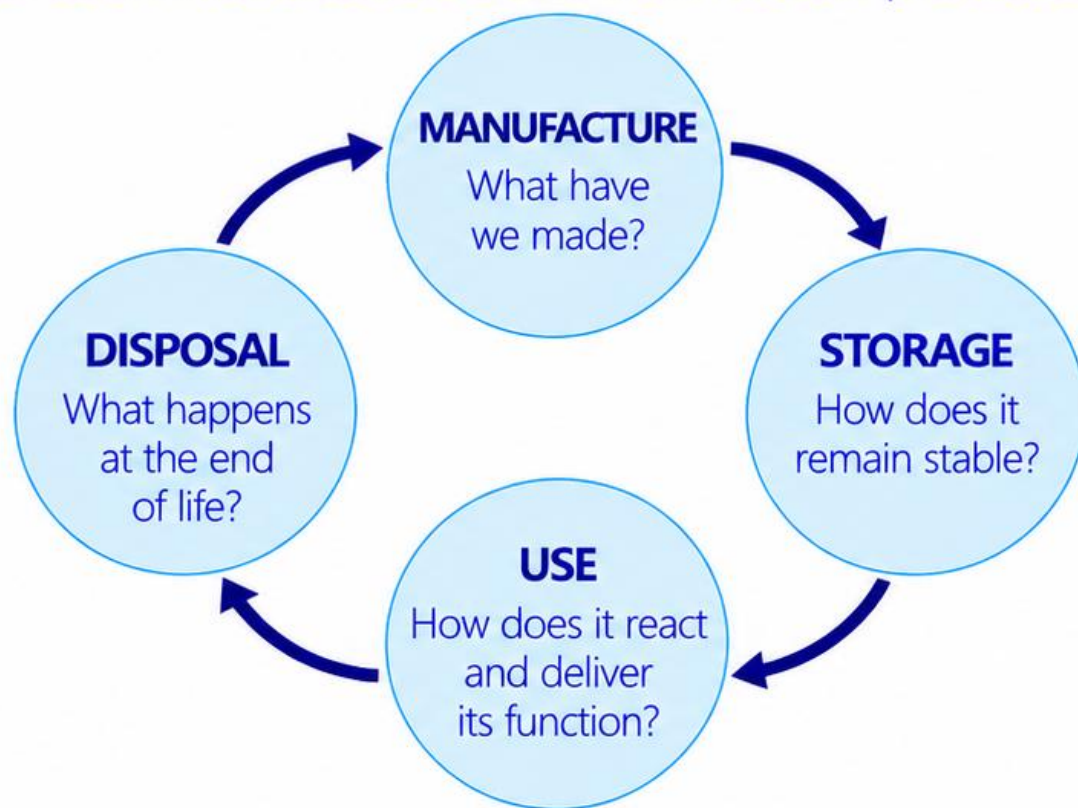
Structure allows us to predict the chemistry. Evidence tells us what we actually made.



From manufacture to the rest of the lifecycle

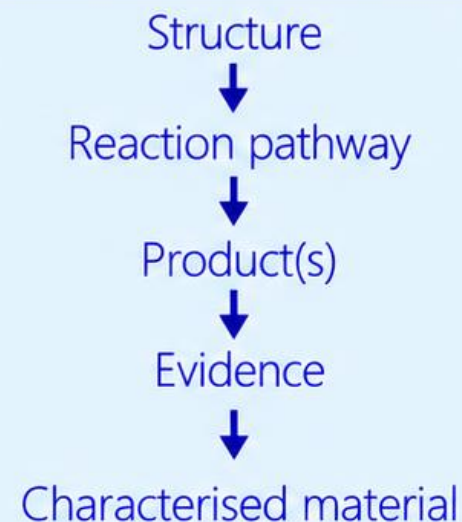
Session 1 has focused on the first part of the lifecycle:

what material has been manufactured and how we can predict and test its composition.



Session 1:

What have we made?



Next:

From Formulation Composition to Chemical Energy Release

How does the composition of an OME material or formulation determine its possible reaction products and the amount of chemical energy released?

