

#### CAIE Chemistry A-level Topic 30 - Hydrocarbons (A level only) Flashcards

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#### Describe the bromination of benzene







#### Describe the halogenation of benzene

Benzene only reacts with bromine if a halogen carrier,  $FeBr_3$  or  $AlBr_3$ , is present.

The reaction forms bromobenzene and hydrogen bromide:

$$C_6H_6 + Br_2 \rightarrow C_6H_5Br + HBr$$







# What is the role of the halogen carrier in the halogenation of benzene?







## What is the role of the halogen carrier in the halogenation of benzene?

The halogen carrier generates the electrophile:

$$Br_2 + FeBr_3 \rightarrow FeBr_4^- + Br^+$$

FeBr<sub>4</sub><sup>-</sup> then reacts with the proton expelled from the intermediate to regenerate the halogen carrier catalyst:

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$$\mathsf{FeBr}_4^- + \mathsf{H}^+ \rightarrow \mathsf{FeBr}_3^- + \mathsf{HBr}_3^-$$

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# Draw and name the mechanism for the bromination of benzene

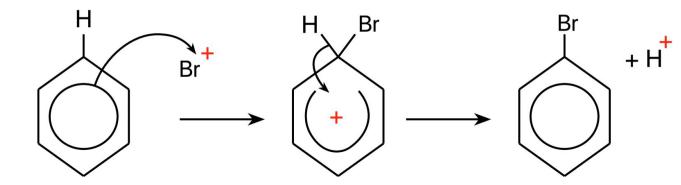






Draw and name the mechanism for the bromination of benzene

**Electrophilic substitution** 



The Br<sup>+</sup> ion accepts a pair of electrons from the ring of delocalisation. The intermediate is so unstable that it breaks down, releasing a hydrogen ion. This forms the product, bromobenzene.







#### How does benzene undergo nitration?







#### How does benzene undergo nitration?

Benzene reacts with conc. nitric acid at a temperature of 50°C - 60°C with a conc. sulfuric acid catalyst to from nitrobenzene and water:

#### $C_6H_6 + HNO_3 \rightarrow C_6H_5NO_2 + H_2O$







## How does sulfuric acid act as a catalyst in the nitration of benzene?







## How does sulfuric acid act as a catalyst in the nitration of benzene?

Sulfuric acid generates the electrophile:

$$H_2SO_4 + HNO_3 \rightarrow NO_2^+ + HSO_4^- + H_2O_4^-$$

Sulfuric acid is regenerated when the hydrogen sulfate ion reacts with the proton that is expelled from the intermediate:

$$HSO_4^- + H^+ \rightarrow H_2SO_4^-$$

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# Draw and name the mechanism for the nitration of benzene

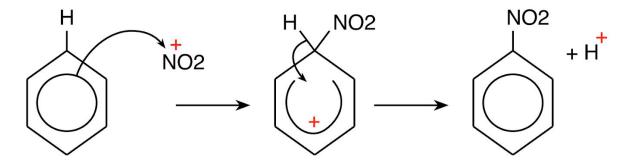






## Draw and name the mechanism for the nitration of benzene

#### **Electrophilic substitution**



The NO<sup>2+</sup> ion accepts a pair of electrons from the delocalised pi system. The intermediate is so unstable that it breaks down, releasing a hydrogen ion. This forms the product, nitrobenzene.







#### How does benzene undergo an alkylation reaction? Write an equation for the reaction between benzene and chloroethane







How does benzene undergo an alkylation reaction? Write an equation for the reaction between benzene and chloroethane

React benzene with a halogenoalkane in the presence of a halogen carrier (e.g.  $AICI_3$ ):

$$C_6H_6 + C_2H_5CI \rightarrow C_6H_5(C_2H_5) + HCI$$







#### How does the halogen carrier generate the electrophile when benzene reacts with a halogenoalkane?







### How does the halogen carrier generate the electrophile when benzene reacts with a halogenoalkane?

The halogen carrier reacts with halogenoalkane to generate the electrophile:

$$AICI_3 + C_2H_5CI \rightarrow AICI_4 + C_2H_5^+$$

AICl<sub>4</sub><sup>-</sup> then reacts with the proton expelled from the intermediate to regenerate the halogen carrier:

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$$AICI_4^- + H^+ \rightarrow AICI_3 + HCI_3$$

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#### How does benzene undergo an acylation reaction? Write an equation for the reaction between benzene and ethanoyl chloride







How does benzene undergo an acylation reaction? Write an equation for the reaction between benzene and ethanoyl chloride

Reflux benzene with an acyl chloride in the presence of a halogen carrier (e.g. AlCl<sub>3</sub>):

 $C_6H_6 + CH_3COCI \rightarrow C_6H_5COCH_3 + HCI$ 







#### How does the halogen carrier generate the electrophile when benzene reacts with an acyl chloride?







# How does the halogen carrier generate the electrophile when benzene reacts with an acyl chloride?

The halogen carrier reacts with acyl chloride to generate electrophile:

$$AICI_3 + CH_3COCI \rightarrow AICI_4 + CH_3CO^+$$

AICI<sub>4</sub><sup>-</sup> reacts with the proton expelled from the intermediate to regenerate the halogen carrier:

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$$AICI_4^- + H^+ \rightarrow AICI_3 + HCI$$





# How does benzene undergo addition reactions with hydrogen?







How does benzene undergo addition reactions with hydrogen?

$$C_6H_6 + 3H_2 \rightarrow C_6H_{12}$$

- Nickel catalyst
- Heated to around 150°C
- High pressure







# How is the side chain of methylbenzene completely oxidised to give benzoic acid?







How is the side chain of methylbenzene completely oxidised to give benzoic acid?

- Alkyl groups attached to a benzene ring are oxidised fairly easily when heated under reflux with alkaline KMnO<sub>4</sub> solution.
- Dilute sulfuric acid is then added to produce benzoic acid.
- Purple solution  $\rightarrow$  Dark brown precipitate of MnO<sub>2</sub>





# How does the ring of delocalisation affect the reactions of benzene?







## How does the ring of delocalisation affect the reactions of benzene?

- Electron density is relatively low so there is weak attraction to electrophiles.
- This means benzene is unable to undergo electrophilic addition reactions and will slowly undergo electrophilic substitution reactions.
- If benzene was to undergo addition reactions it would permanently break the delocalisation energetics do not favour this reaction.







#### How can you tell whether a substitution reaction by a halogen will occur in the benzene ring or on the side chain?







How can you tell whether a substitution reaction by a halogen will occur in the benzene ring or on the side chain?

For the substitution by a halogen:

- If UV light is present and a catalyst is absent: substitution takes place on the side chain.
- If a catalyst is present and UV light is absent: substitution takes place in the benzene ring.







#### What is a directing effect?







#### What is a directing effect?

#### Substituents on a benzene ring can affect at which position a further substitution reaction might occur on.







# What are the directing effects of the following substituents on a benzene ring: $-NH_2$ , -OH, -R, $-NO_2$ , -COOH and -COR?







What are the directing effects of the following substituents on a benzene ring:  $-NH_2$ , -OH, -R,  $-NO_2$ , -COOH and -COR?

- $-NH_2$  directs to positions 2, 4 and 6
- -OH -directs to positions 2, 4 and 6
- -R directs to positions 2, 4 and 6
- -NO<sub>2</sub> -directs to position 3 and 5
- -COOH directs to position 3 and 5
- -COR directs to position 3 and 5



