

Benzene Properties

A Level



Part A Benzene

Which property of benzene may be directly attributed to the stability associated with its delocalised electrons?

- ☐ Its enthalpy change of formation is negative.
 - ☐ It has a low boiling point.
 - ☐ It is susceptible to attack by nucleophilic reagents.
 - ☐ It tends to undergo substitution rather than addition reactions.
 - ☐ It does not conduct electricity.
-

Part B Reactions

The most characteristic type of reaction undergone by benzene and its derivatives is:

- ☐ Electrophilic addition
 - ☐ Free radical substitution
 - ☐ Nucleophilic substitution
 - ☐ Nucleophilic addition
 - ☐ Electrophilic substitution
-



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Nitration of Methylbenzene

A Level
P P P

When methylbenzene reacts with a mixture of concentrated nitric and sulfuric acids the product consists largely of two isomers of formula $C_7H_7NO_2$.

Part A Reaction type

What type of reaction is this?

Part B Major products

While the nitro group could replace any of the hydrogens on the ring, giving potential isomers, not all of them are equally likely. Due to the directing effect of the methyl group, the main products will be 1-methyl--nitrobenzene and 1-methyl--nitrobenzene.

Items:

- 1
- 2
- 3
- 4
- 5

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Nitration of Benzene Mechanism

A Level



The mechanism of the nitration of benzene by concentrated nitric and sulfuric acids is thought to proceed *via* the following pathway.

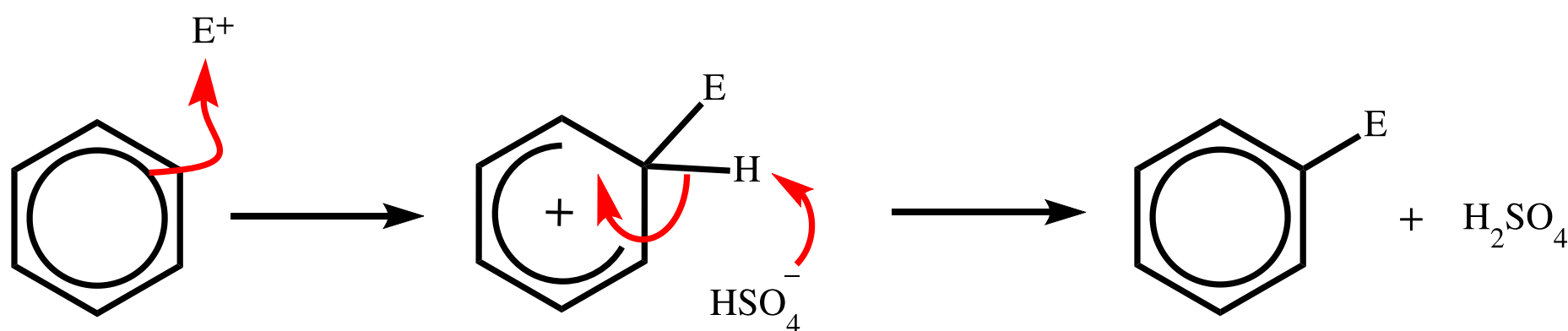


Figure 1: Benzene nitration mechanism

Part A Electrophile

What is the formula and charge of the electrophile in this reaction?

Part B Formation of electrophile

Write a balanced equation for the formation of this electrophile (state symbols are not required).

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Aromatic Chemistry with Side Chains

Part A Reaction with cyanide ion

A compound **Q** has the following structure:

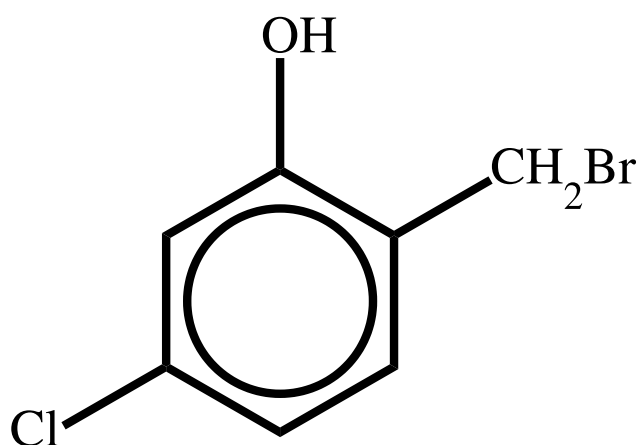
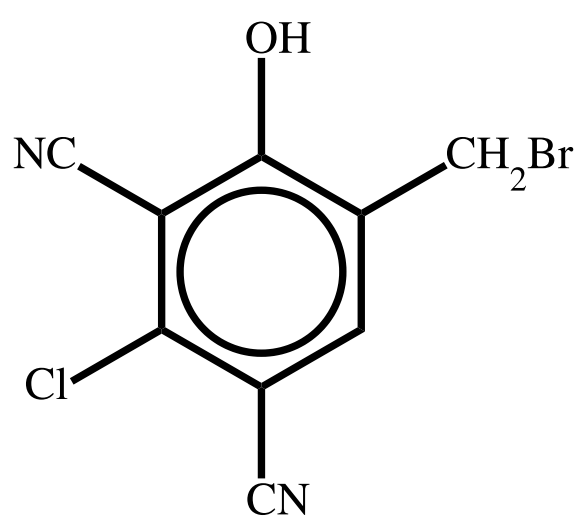
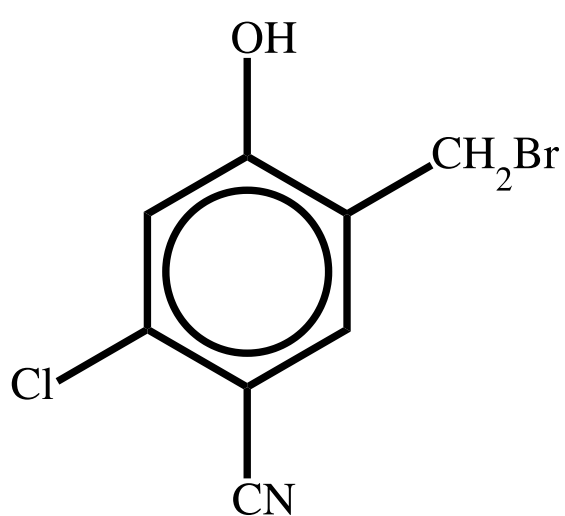


Figure 1: Structure of compound **Q**

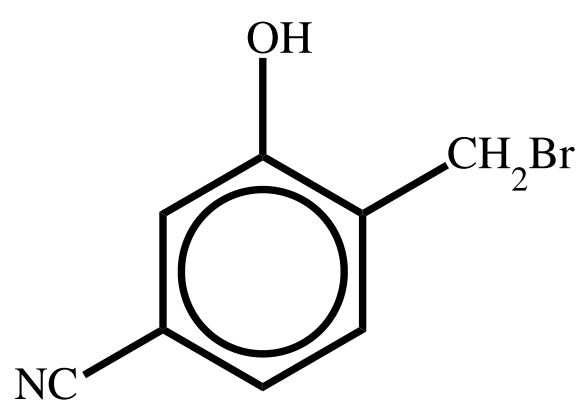
Which compound is obtained by nucleophilic substitution when a cyanide ion reacts with compound **Q**?



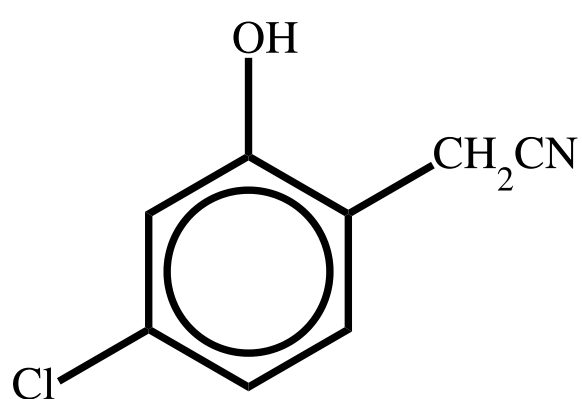
A



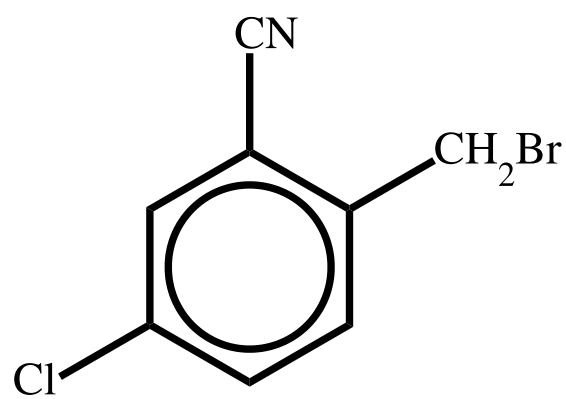
B



C



D



E

Figure 2: Possible reaction products of **Q** with cyanide ion.

☐ **A**

☐ **B**

☐ **C**

☐ **D**

Part B **Methylbenzene with chlorine**

The reaction between boiling methylbenzene and chlorine takes place in a number of steps to give several products.

Which of the following could be one of the steps?

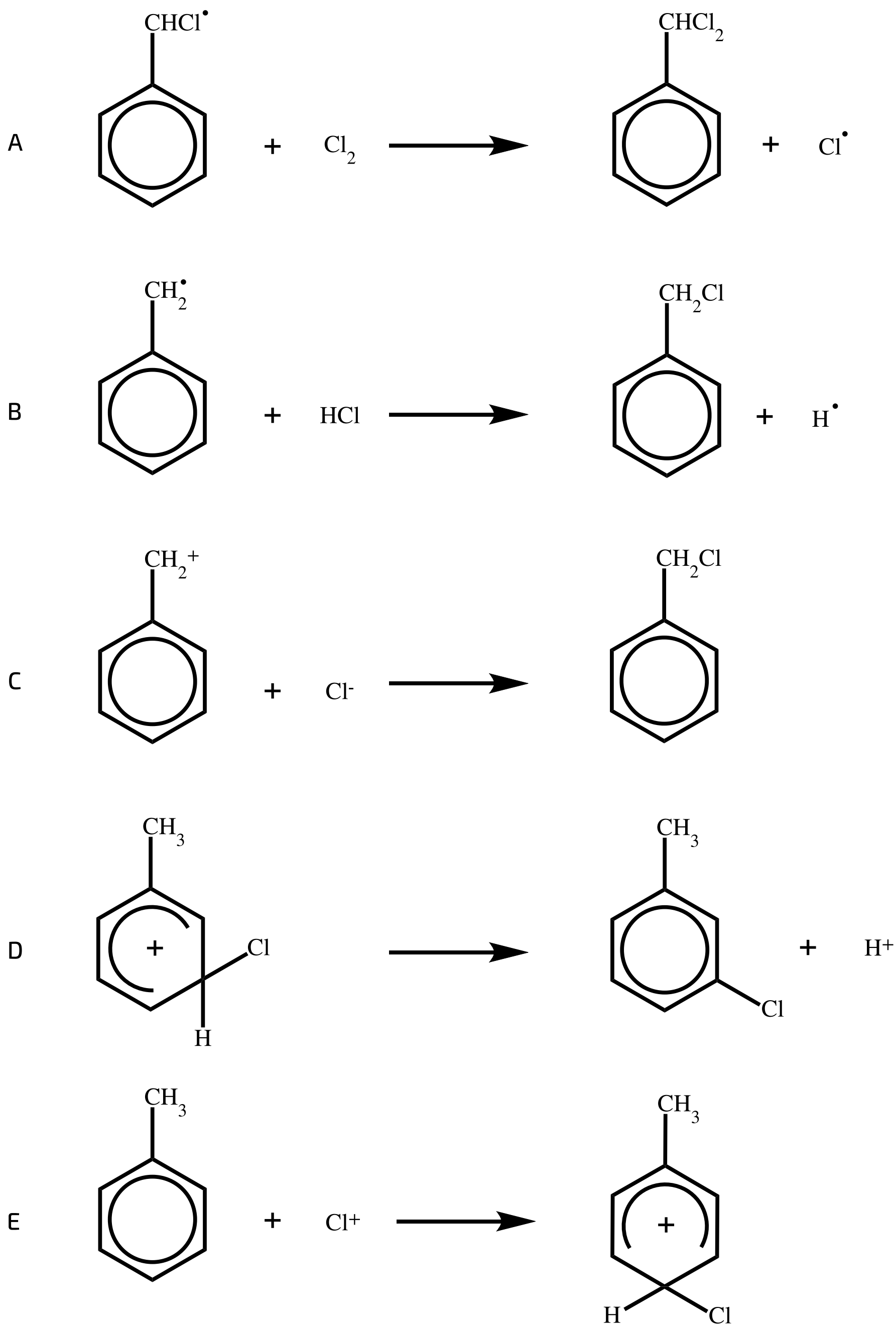


Figure 3: Possible reaction steps of methylbenzene with chlorine.

Phenols

A Level



Part A Phenol with aqueous bromine

An account in a student's notebook read:

"An excess of aqueous bromine was added to aqueous phenol in a test-tube. 2,4,6-Tribromophenol was produced as a creamy-white precipitate suspended in a yellow alkaline solution."

Which statement in this account must have been incorrect?

- ☐ The precipitate obtained is not creamy-white but yellow
 - ☐ The precipitate is not 2,4,6-tribromophenol, but a mixture of 2- and 4-bromophenol
 - ☐ The resultant solution is not alkaline, but acidic.
 - ☐ The resultant solution is not yellow, but purple.
-

Part B Germicide

Phenol was one of earliest antiseptics used; however, it causes painful blisters on the skin. A safer and more effective germicide can be produced by reacting phenol with aqueous chlorine.

What is the formula of this safer germicide?

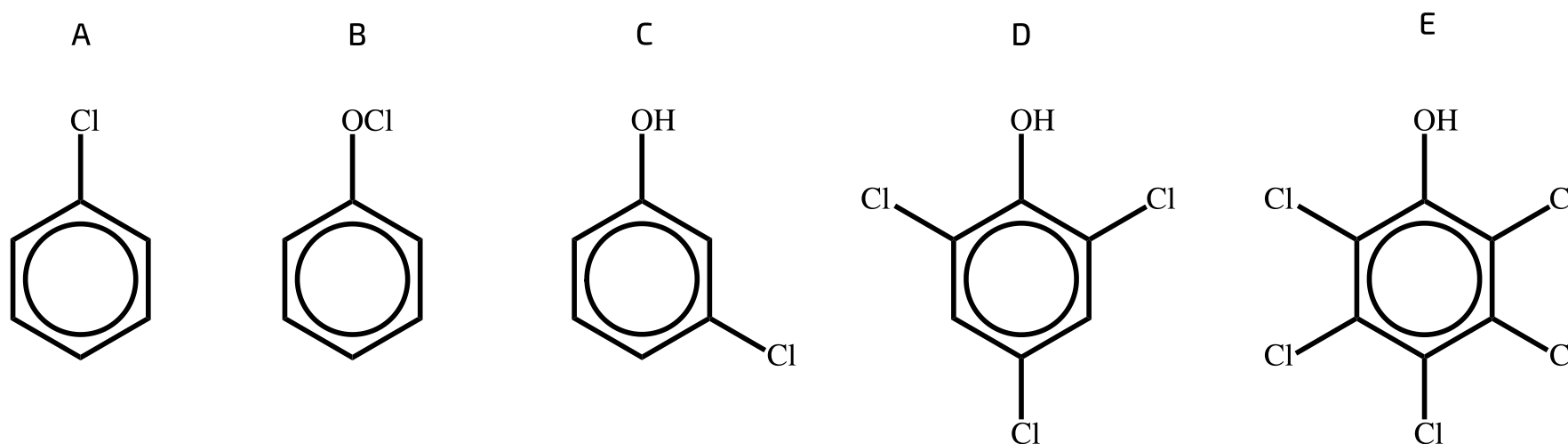


Figure 1: Possible products of reaction between phenol and chlorine

- ☐ A
- ☐ B
- ☐ C
- ☐ D
- ☐ E

Part A adapted with permission from UCLES, A-Level Chemistry, June 1995, Paper 4, Question 25;

Part B adapted with permission from UCLES, A-Level Chemistry, November 1992, Paper 4, Question 25.

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Aromatics with Nitrogen Groups

A Level



Part A Phenylamine and benzoyl chloride

What is the most likely product of the reaction between phenylamine and benzoyl chloride ($\text{C}_6\text{H}_5\text{COCl}$)?

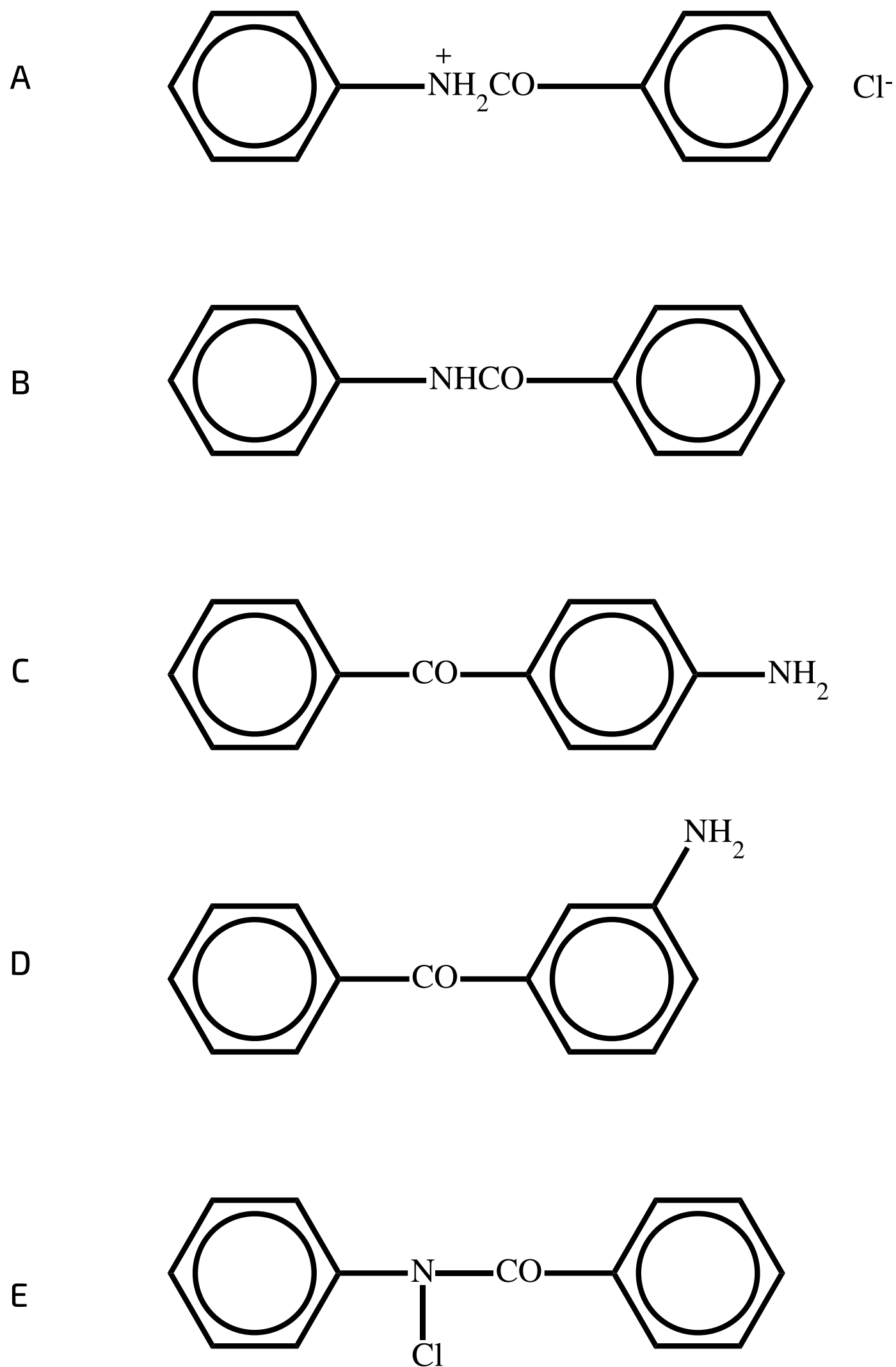


Figure 1: Possible products of reaction between phenylamine and benzoyl chloride.

- ☐ A
- ☐ B
- ☐ C

Part B Hydrolysis

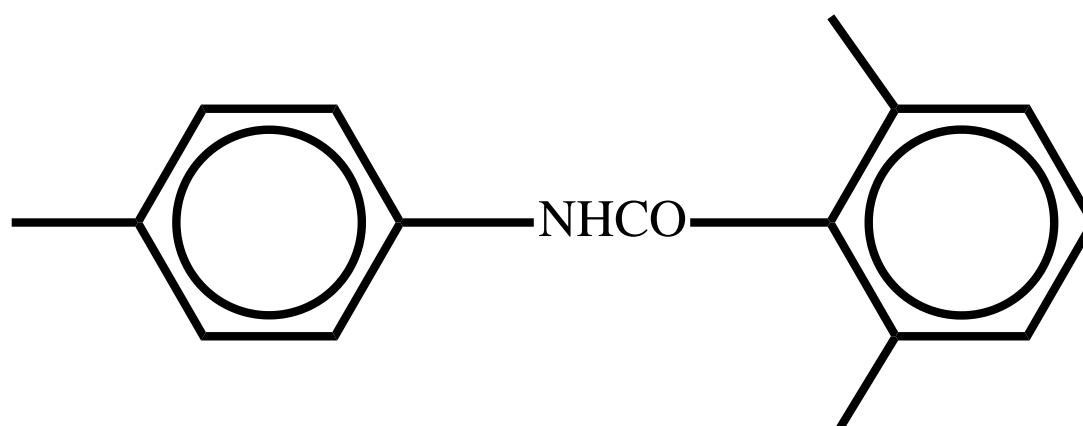


Figure 2: Compound Y

Which of the following are formed by the hydrolysis of compound Y?

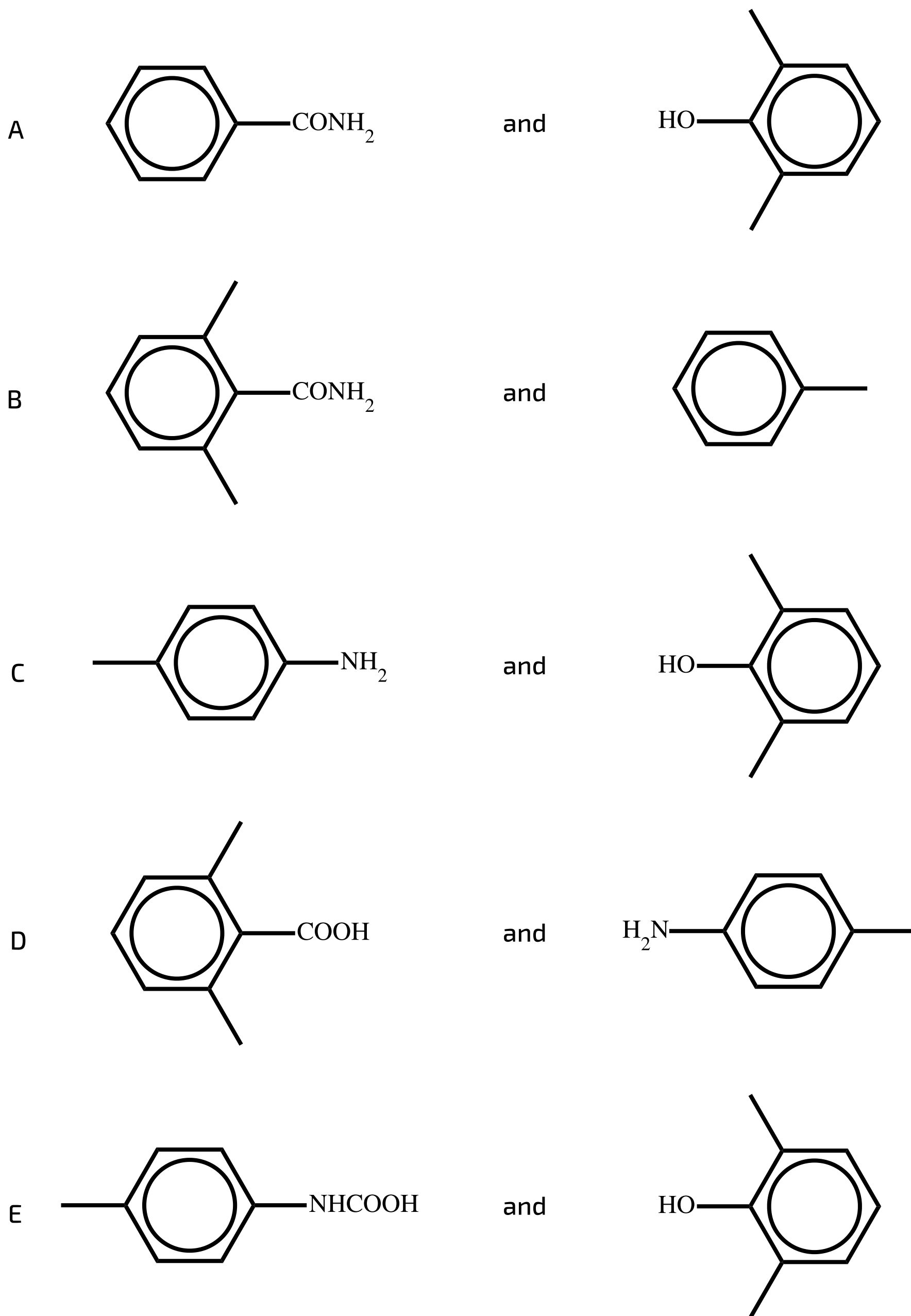


Figure 3: Possible products of hydrolysis of compound Y

☐ A

☐ B

Electrophilic Attack

A Level



Part A Site of attack

At which of the carbon atoms in the molecule below is electrophilic attack most likely?

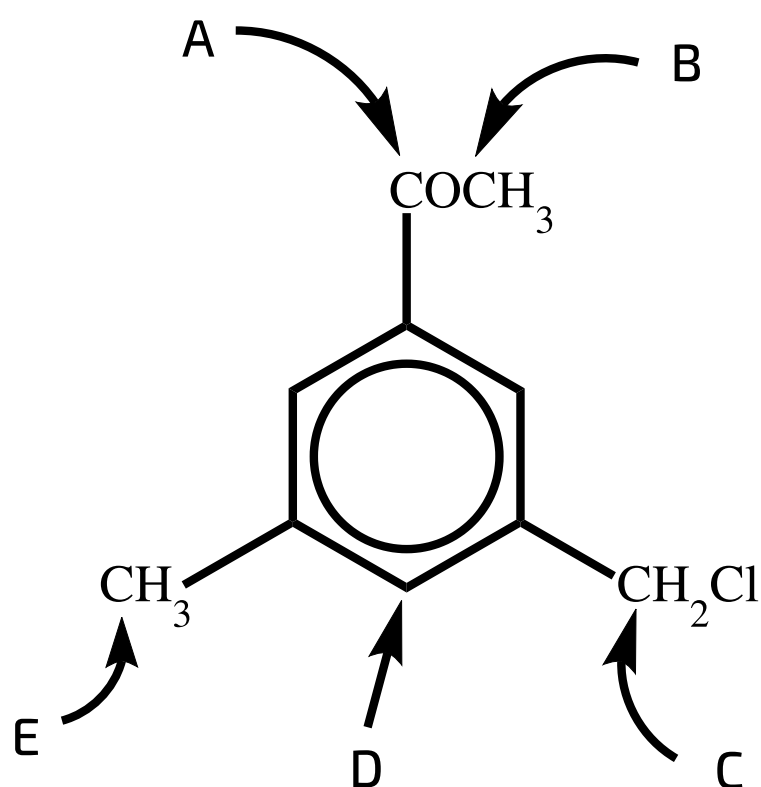


Figure 1: Potential sites of electrophilic attack

- ☐ A
- ☐ B
- ☐ C
- ☐ D
- ☐ E

Part B Cumene process

The first stage of the cumene process for the industrial production of phenol is as follows.

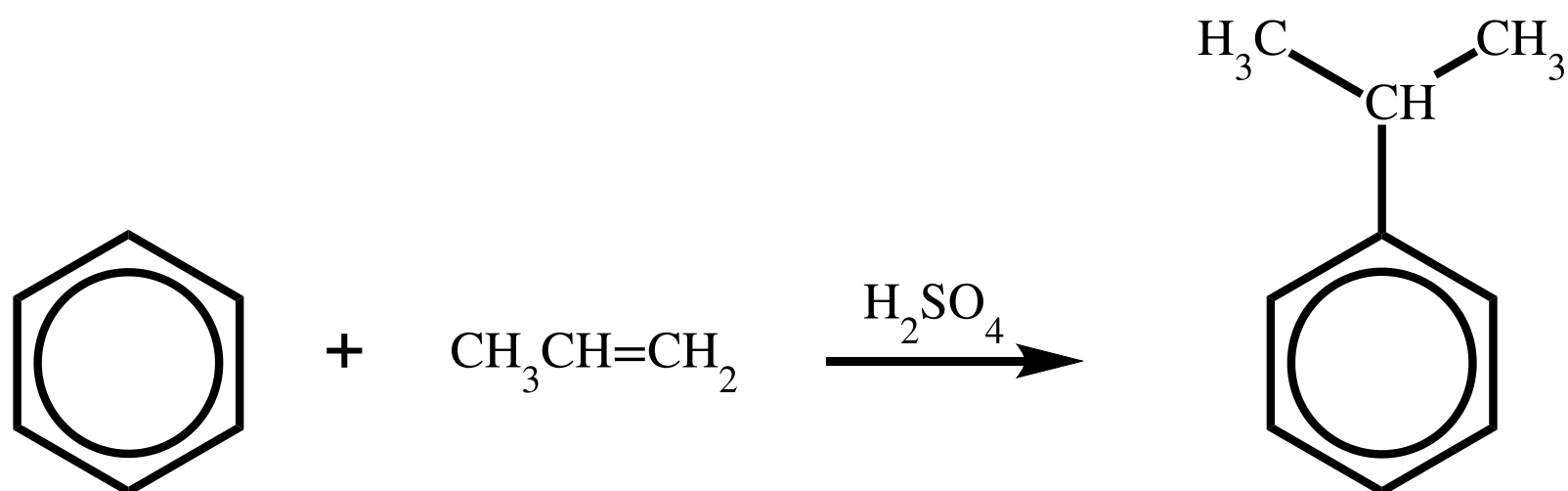
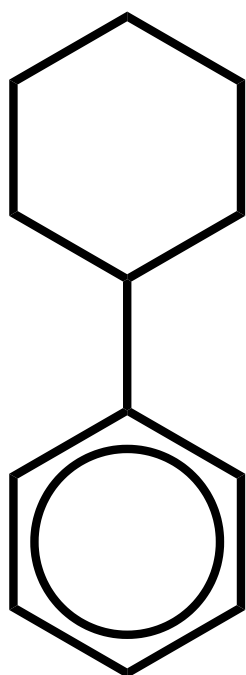
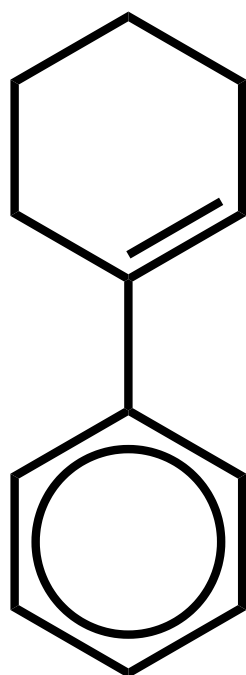


Figure 2: First stage of the cumene process

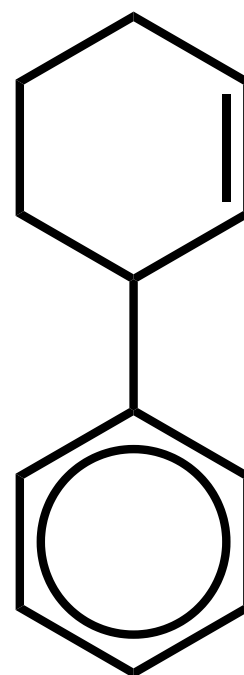
Which of the following would be the product of the reaction, under similar conditions, between benzene and cyclohexene?



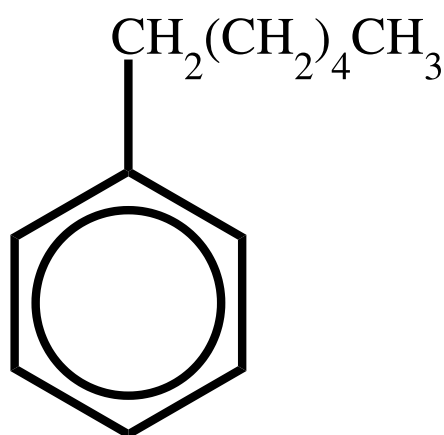
A



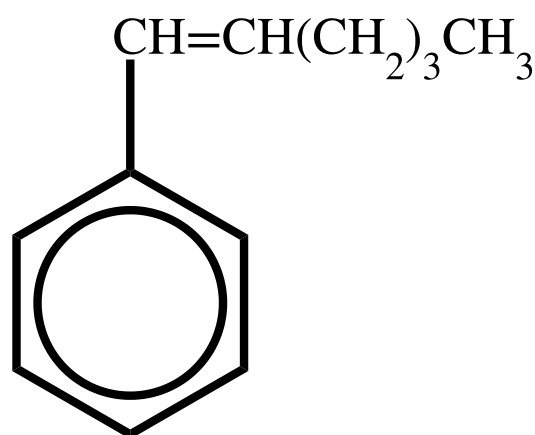
B



C



D



E

Figure 3: Possible products of the reaction between benzene and cyclohexene



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Reactions of Aromatics

A Level



Draw the structures of the products of the following reactions. If there is no reaction, give the structure of the starting material.

Use the [structure editor](#) to generate SMILES strings.

In the editor, after drawing your structure, click on the round, yellow smiley face to generate a SMILES string. Copy the SMILES string and paste it in the answer box.

[Using the structure editor](#)

Part A Benzene + Br₂

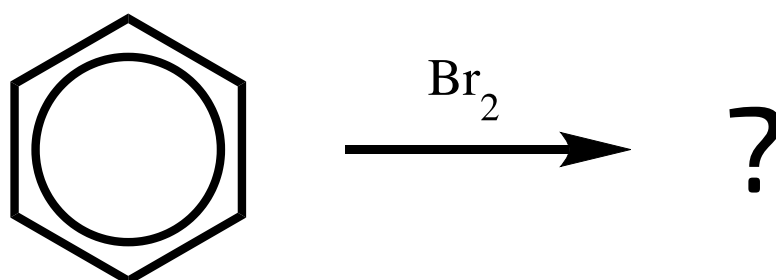


Figure 1: Benzene + Br₂

Part B Benzene + Br₂ / FeBr₃

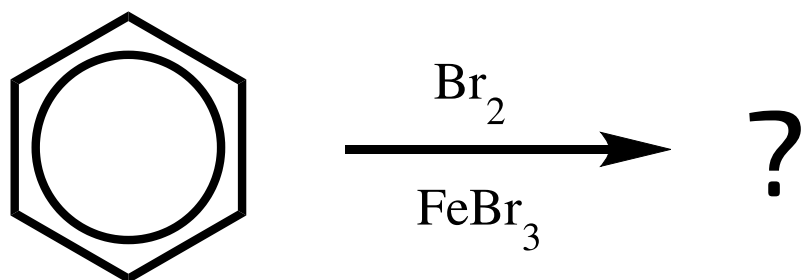


Figure 2: Benzene + Br₂ / FeBr₃

Part C Phenol + Br₂

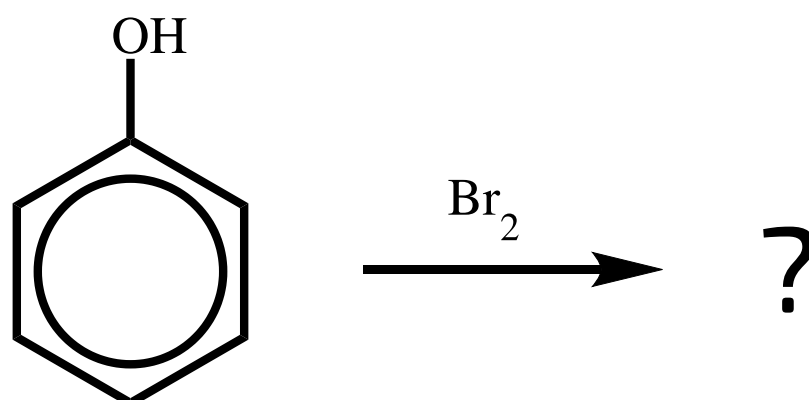


Figure 3: Phenol + Br₂

Part D Benzene + CH₃COCl / AlCl₃

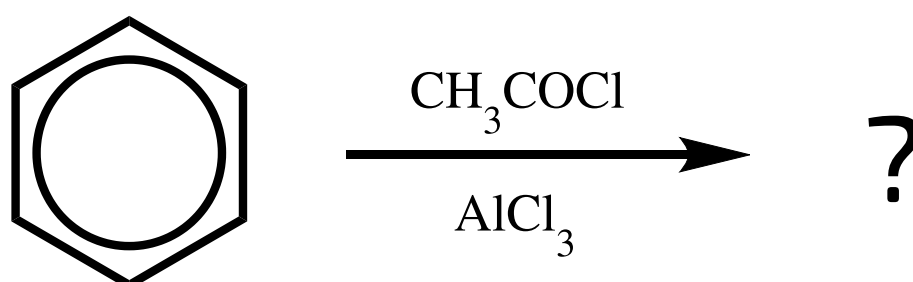


Figure 4: Benzene + CH₃COCl / AlCl₃

Part E Phenol + CH_3COCl

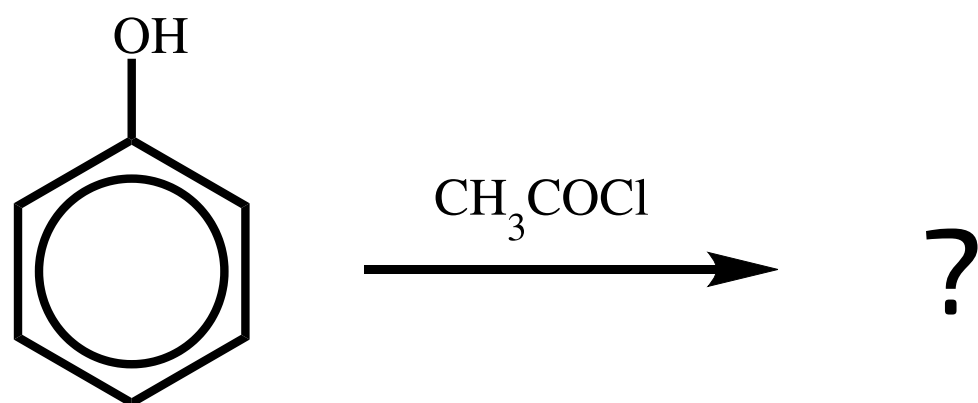


Figure 5: Phenol + CH_3COCl

Part F Nitrobenzene + Sn / HCl

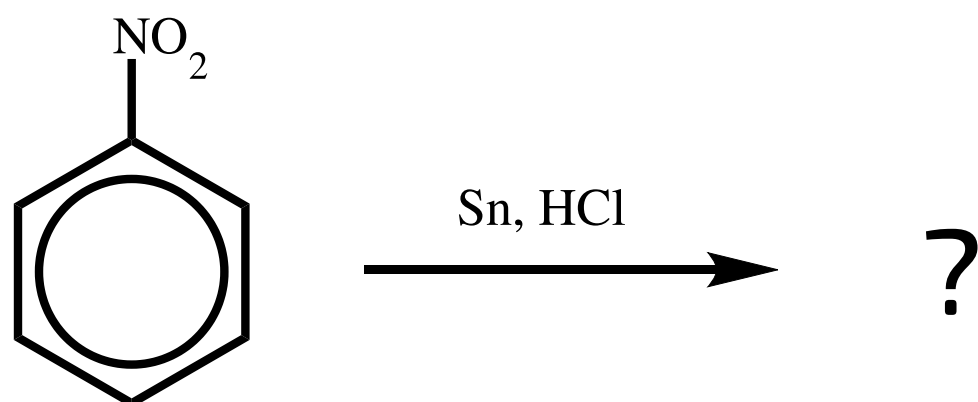


Figure 6: Nitrobenzene + Sn / HCl

Part G Benzene + $\text{C}_2\text{H}_5\text{Cl}$ / AlCl_3

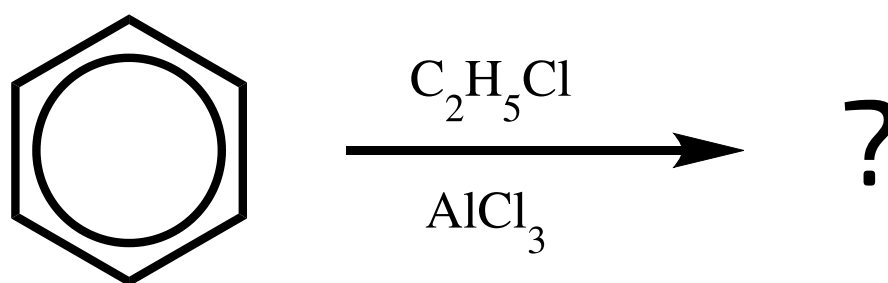


Figure 7: Benzene + $\text{C}_2\text{H}_5\text{Cl}$ / AlCl_3

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Ethylbenzene

A Level



Ethylbenzene, is an important intermediate in the manufacture of poly(phenylethene), commonly known as polystyrene.

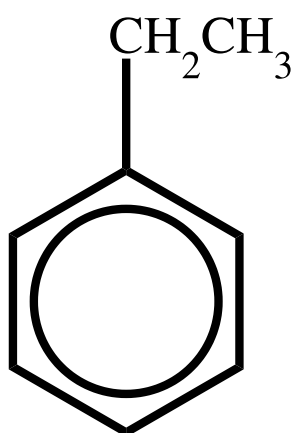


Figure 1: Structure of ethylbenzene.

When ethylbenzene is treated with chlorine under certain conditions, a mixture of two isomeric chlorides, **C** and **D**, are formed.

C and **D** both react with hot concentrated alcoholic potassium hydroxide to give phenylethene, but with aqueous sodium hydroxide, form two isomeric compounds **E** and **F**, respectively, of formula $C_8H_{10}O$.

E reacts with acidified potassium dichromate(VI) to give **G** which does not give a silver mirror in the presence of Tollens' reagent.

F also reacts with acidified potassium dichromate(VI) to give **H** as a final product. **H** gives effervescence of CO_2 on addition of aqueous sodium carbonate solution.

Give the structures of compounds **C** - **H** . Use the [structure editor](#) to generate a SMILES string as your answer.

Part A Compound C

Give the structure of compound **C**. Use the [structure editor](#) to generate a SMILES string as your answer.

Part B **Compound D**

Give the structure of compound **D**. Use the [structure editor](#) to generate a SMILES string as your answer.

Part C **Compound E**

Give the structure of compound **E**. Use the [structure editor](#) to generate a SMILES string as your answer.

Part D **Compound F**

Give the structure of compound **F**. Use the [structure editor](#) to generate a SMILES string as your answer.

Part E **Compound G**

Give the structure of compound **G**. Use the [structure editor](#) to generate a SMILES string as your answer.

Part F **Compound H**

Give the structure of compound **H**. Use the [structure editor](#) to generate a SMILES string as your answer.

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Aromatic Acids and Bases

A Level



The benzene ring has a strong effect on the acidity and basicity of groups directly bonded to the ring. **Negative charges** and **lone pairs** of electrons are **delocalised** into the aromatic ring.

OH groups become more acidic and N lone pairs become less basic as a result of this delocalisation.

Part A Aromatic acids

Match the aromatic compound with its correct pK_a value.

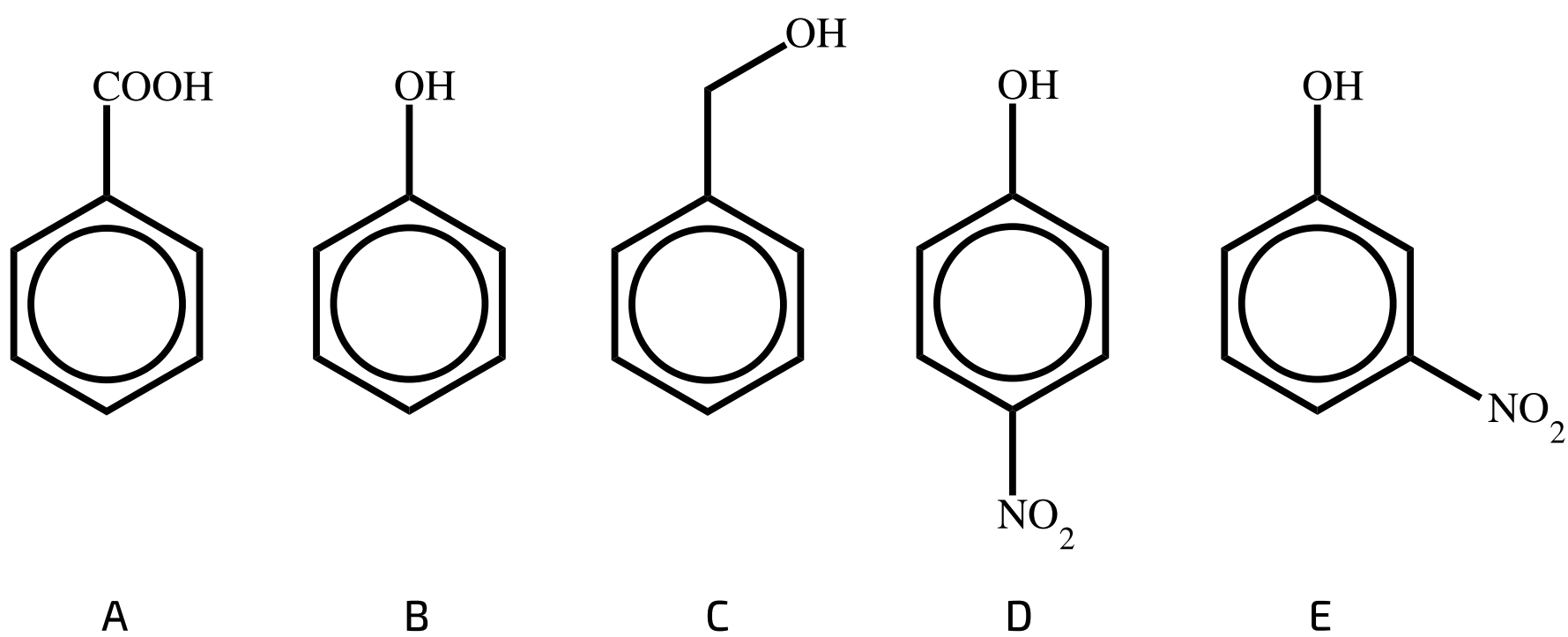


Figure 1: Aromatic compounds A - E with acidic hydrogen atoms.

Compound	pK_a
A	<input type="text"/>
B	<input type="text"/>
C	<input type="text"/>
D	<input type="text"/>
E	<input type="text"/>

Items:

- 4.2
- 7.2
- 8.4
- 10.0
- 15.4

Part B Phenylamine with aqueous sulfuric acid

Which of the following products is formed when phenylamine (aniline) dissolves in dilute aqueous sulfuric acid?

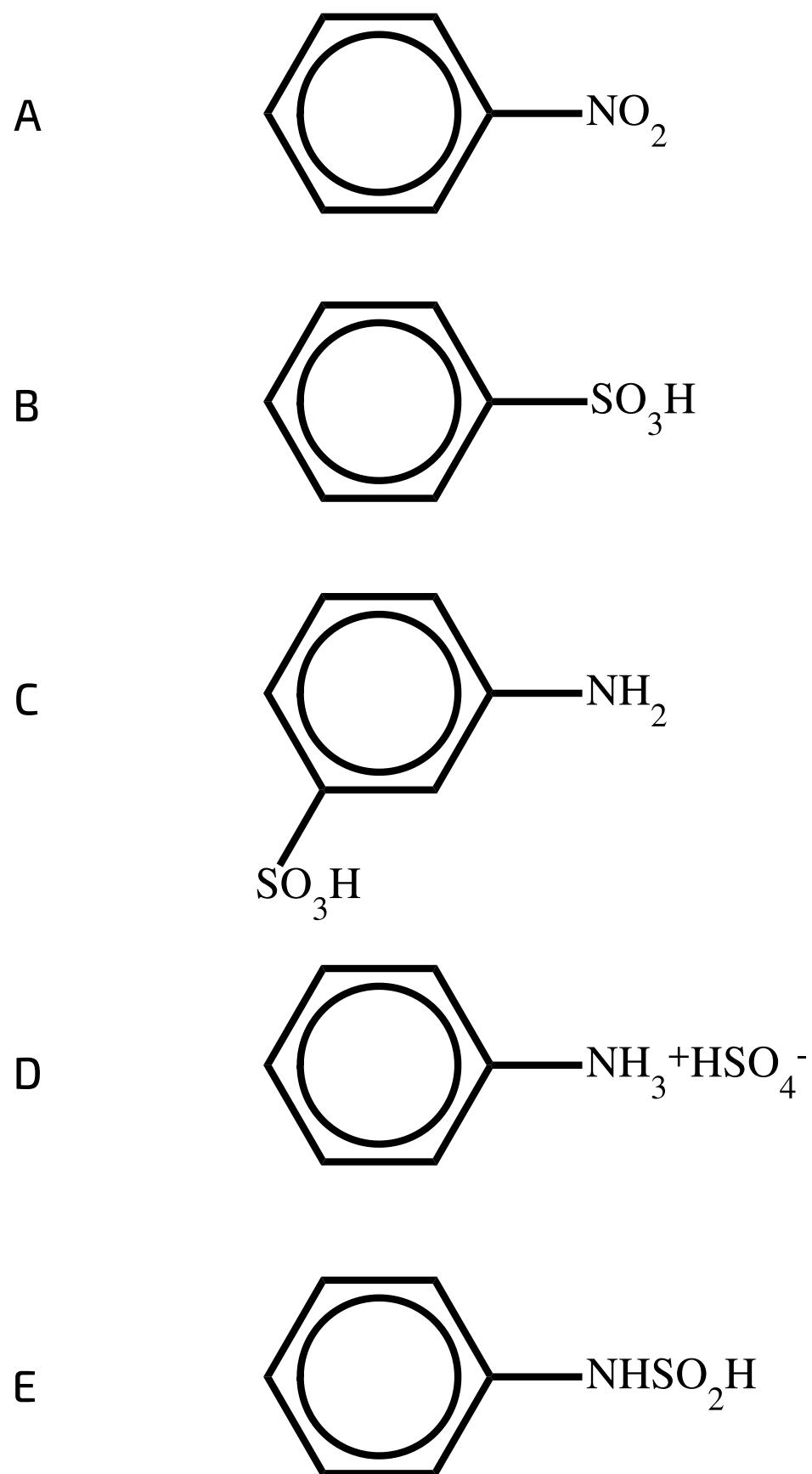


Figure 2: Possible products of phenylamine with dilute aqueous sulfuric acid.

- ☐ A
- ☐ B
- ☐ C
- ☐ D
- ☐ E

Part C Basicity of amines

Rank the following compounds in order of increasing basicity:

Most basic
<input type="text"/>
<input type="text"/>
<input type="text"/>
<input type="text"/>
<input type="text"/>
<input type="text"/>
Least basic

Items:

Ammonia

Ethylamine

Diphenylamine

Phenylamine

Diethylamine

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Part B adapted with permission from OCSEB, A-Level Chemistry, June 1994, Paper 1, Question 28

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