

5.3.2 Draw aromatic substitution and regenerate the catalyst

Name: _____ Class: _____ Date: _____

Total: 34 marks

KEY WORDS evidence • conditions

Objective

Draw aromatic substitution and regenerate the catalyst. All questions and marking guidance are original.

1 Key knowledge and worked examples

Curly arrows start at an electron pair and end where that pair moves. In nitration, the ring attacks NO_2^+ . A positive intermediate contains H and NO_2 on the same carbon; the C–H pair restores the ring as H^+ leaves. Sulfuric acid is regenerated.

■ Worked method

$\text{HNO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{NO}_2^+ + \text{HSO}_4^- + \text{H}_2\text{O}$. After ring substitution, HSO_4^- accepts the released proton and regenerates H_2SO_4 . In acylation, $\text{RCOCl} + \text{AlCl}_3 \rightarrow \text{RCO}^+ + \text{AlCl}_4^-$. Reaction of the substituted intermediate with AlCl_4^- gives HCl and restores AlCl_3 .

2 Practice

2.1 Draw the ring attack, positive intermediate and ring-restoration electron-pair arrows for benzene nitration after NO_2^+ is generated. [4]

2.2 State which reagent generates the nitrating electrophile with nitric acid, and which species accepts H^+ to regenerate that reagent. [2]

2.3 Write the equations for ethyl-electrophile generation using $\text{C}_2\text{H}_5\text{Cl}/\text{AlCl}_3$ and catalyst regeneration using $\text{AlCl}_4^-/\text{H}^+$, using the simple free-electrophile model. [2]

3 Exam-style questions

3.1 Write ethanoyl-electrophile generation and the overall benzene acylation equation with ethanoyl chloride. Identify the organic product. [3]

3.2 Explain why phenol bromination is faster than benzene under bromine-water conditions and give the balanced overall equation. [3]

3.3 A proposed arrow starts at NO_2^+ and ends inside benzene, followed by an arrow from H^+ into the ring. Correct both electron-flow errors. [2]

3.4 Draw ring attack, the positive intermediate and ring-restoration electron-pair arrows for benzene bromination using $\text{Br}_2/\text{FeBr}_3$. Include electrophile generation and catalyst regeneration in the simple electrophile model. [6]

3.5 Draw ring attack, the positive intermediate and ring-restoration electron-pair arrows for benzene alkylation using $\text{C}_2\text{H}_5\text{Cl}/\text{AlCl}_3$. Include electrophile generation and catalyst regeneration in the simple electrophile model. [6]

3.6 Draw ring attack, the positive intermediate and ring-restoration electron-pair arrows for benzene acylation using $\text{CH}_3\text{COCl}/\text{AlCl}_3$. Include electrophile generation and catalyst regeneration in the simple electrophile model. [6]
