II.2 Reaction Mechanisms

Civil Services 2016–2026: **7** parts, **55** marks · IFoS 2016–2025: **12** parts, **80** marks

Syllabus. General methods (both kinetic and non-kinetic) of study of mechanism of organic reactions: isotopic method, cross-over experiment, intermediate trapping, stereochemistry; energy of activation; thermodynamic control and kinetic control of reactions.

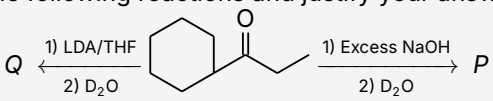
Marks	2016	2017	2018	2019	2020	2021	2022	2023	2024	2025	2026
CSE	0	0	0	0	0	10	0	15	20	10	0
IFoS	5	20	5	10	0	0	10	10	10	10	

How to use this chapter. Read every question once and mark the ones that repeat. Pick three, write them by hand against the clock (about 7 minutes for 10 marks), then compare with the model answers on vkcscience.com.

2025

CSE 2025 · Q4(c)(ii) Kinetic and thermodynamic enolates trapped with D_2O [10 marks]

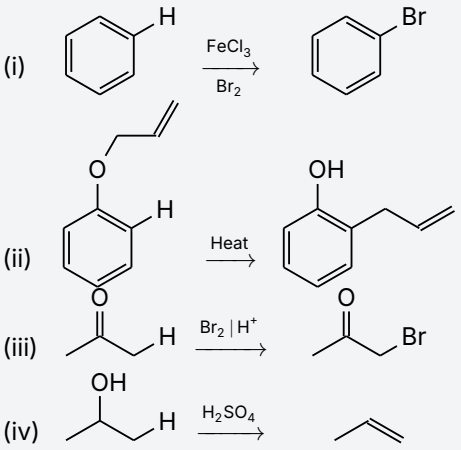
(ii) Identify the major product in the following reactions and justify your answer:



[10]

IFoS 2025 · Q4(a) Primary kinetic isotope effect [10 marks]

Identify the reaction from the following reactions (i – iv) that shows primary kinetic isotope effect for the H-atom (C – H) and show the mechanism of the reaction to identify the rate limiting step :



2024

CSE 2024 · Q2(a)(i) kH/kD = 7.1 for 2-phenylethyl bromide with ethoxide [10 marks]

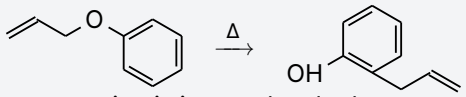
(i) Consider the following reactions:

$$C_6H_5{-}CH_2{-}CH_2Br \xrightarrow[\text{Rate} = k_H]{EtO^-} C_6H_5{-}CH{=}CH_2 \qquad C_6H_5{-}CD_2{-}CH_2Br \xrightarrow[\text{Rate} = k_D]{EtO^-} C_6H_5{-}CD{=}CH_2$$

It was observed that k_H/k_D = 7·1. Based on this data, predict the mechanism and justify your answer. 10

CSE 2024 · Q4(b)(i) Crossover experiment for the Claisen rearrangement [10 marks]

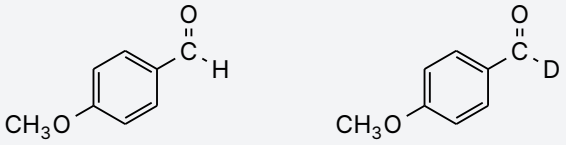
(i) Consider the following reaction:



How would you confirm that the above reaction is intramolecular by crossover experiment? 10

IFoS 2024 · Q1(b) Secondary kinetic isotope effect [5 marks]

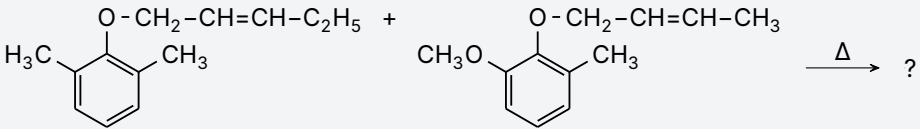
What is secondary kinetic isotope effect? Explain it using the reaction of HCN with the following molecules :



I II

IFoS 2024 · Q2(a)(i) A para-Claisen crossover experiment [5 marks]

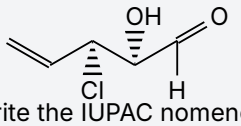
(i) Indicate the product(s) in the following reaction. What information is obtained about the reaction mechanism from the product(s) observed?



2023

CSE 2023 · Q1(b)(i) IUPAC name with stereodescriptors [5 marks]

(i)



Write the IUPAC nomenclature of the above compound by assigning the stereochemistry. (5 marks)

CSE 2023 · Q2(a)(ii) Primary and secondary kinetic isotope effects [5 marks]

(ii) (A) $PhCH_2-H^* + Br^\bullet \longrightarrow PhCH_2^\bullet + {}^*H-Br$

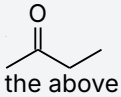
(B) $p-MeOC_6H_4-CH^*O + HCN \longrightarrow p-MeOC_6H_4-CH^*(OH)CN$

(C) 9,10-dihydro-9,10-ethanoanthracene (H^* on the bridge) $\longrightarrow$ anthracene + $CH_2=CHH^*$

(D) cyclopentyl-NMe_3^+ (H^* on C-2) + $\overset{\ominus}{O}H \longrightarrow$ cyclopentene + Me_3N + H^*-OH

Identify the above reactions that show primary kinetic isotope effect and secondary kinetic isotope effect. (5 marks)

CSE 2023 · Q2(a)(iii) Enolates of butan-2-one: NaOMe versus LDA [5 marks]

(iii) (A) $\xleftarrow[MeOH]{NaOMe}$  $\xrightarrow[THF,\ -78\ °C]{LDA}$ (B)

Identify (A) and (B) in the above reactions and explain the mechanism. (5 marks)

IFoS 2023 · Q1(b) Evidence for a tetrahedral intermediate [5 marks]

With the help of the isotopic labelling experiment, how will you establish that $B_{Ac}2$ mechanism of ester hydrolysis involves true intermediate, not a transition state ?

IFoS 2023 · Q3(d) Racemization during alpha bromination [5 marks]

Base catalysed bromination of optically active ketone results in racemization of product. How will you account for this observation ?

2022

IFoS 2022 · Q1(c) Tracing the nitrile carbon [5 marks]

Establish the origin of carbon in the cyano group of the product obtained in the following reaction by using isotopic labelling method:

$$R{-}COO^- + BrCN \longrightarrow R{-}CN + Br^- + CO_2$$

IFoS 2022 · Q2(e) Deuterium and hydrolysis rate [5 marks]

The compounds *A* and *B* undergo hydrolysis in the presence of water. Compare their hydrolysis behaviour giving appropriate explanation:

$$\underset{A}{(CH_3)_2CHBr} \qquad \underset{B}{(CD_3)_2CHBr}$$

2021

CSE 2021 · Q1(a) Origin of the CN group in RCOO $^-$ + BrCN [10 marks]

In the reaction

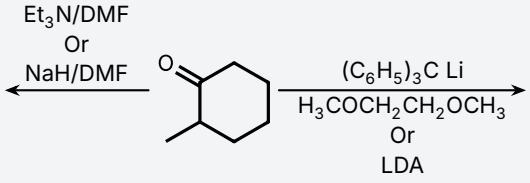
$$R{-}COO^- + Br{-}CN \longrightarrow R{-}CN + Br^- + CO_2\uparrow$$

What is the origin of −CN group in the product? Explain by using isotopic labelling technique.

2019

IFoS 2019 · Q2(a) Kinetic and thermodynamic enolates of 2-methylcyclohexanone [10 marks]

2-Methylcyclohexanone forms an enolate mixture of varied composition when subjected to the following reaction conditions. Draw the structures of the products and identify the major/minor products:



2018

IFoS 2018 · Q1(g) Acetylation of methanol: pyridinium acetate or ketene? [5 marks]

Acetylation of methanol using acetyl chloride and pyridine is proposed to proceed through the following two pathways:

(i) Via formation of pyridinium acetate

(ii) Via formation of ketene

Can you devise an experiment to prove through which pathway the reaction actually proceeds?

2017

IFoS 2017 · Q4(d) Kinetic versus thermodynamic control [10 marks]

With a suitable free-energy profile diagram illustrate and explain what is meant by 'thermodynamically controlled product' and 'kinetically controlled product'.

IFoS 2017 · Q7(c) Crossover experiments in mechanism elucidation [10 marks]

Write a short note on ‘Crossover Experiment’ with special emphasis on the elucidation of reaction mechanism.

2016

IFoS 2016 · Q1(b) Crossover experiments [5 marks]

Discuss the role of crossover experiments in determining the reaction mechanism.