II.6 Addition Reactions

Civil Services 2016–2026: **21** parts, **190** marks · IFoS 2016–2025: **14** parts, **80** marks

Syllabus. Electrophilic addition to C=C and C≡C; nucleophilic addition to C=O, C≡N, conjugated olefins and carbonyls.

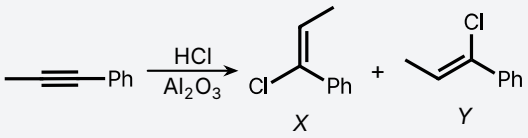
Marks	2016	2017	2018	2019	2020	2021	2022	2023	2024	2025	2026
CSE	0	10	10	0	45	25	10	20	20	40	10
IFoS	10	0	5	0	15	15	5	10	10	10	

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.

2026

CSE 2026 · Q1(d) HCl on 1-phenylpropyne: E/Z, kinetic and thermodynamic products [10 marks]

The following reaction gives two products X and Y:



(i) Assign E/Z configuration to the products X and Y.

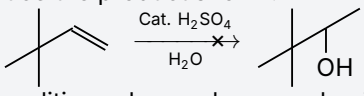
(ii) Between X and Y, identify the kinetic and thermodynamic products.

(iii) Under the reaction conditions, the kinetic product slowly gets converted to a thermodynamic product, until the equilibrium is reached. Propose a probable mechanism for this conversion.

2025

CSE 2025 · Q2(b)(i) Acid-catalysed hydration of 3,3-dimethylbut-1-ene [10 marks]

(i) The following reaction does not produce the product shown:

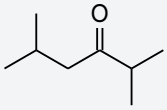


(1) Predict the major product from the conditions shown above, and write a detailed mechanism for its formation.

(2) Write that reaction conditions which would lead to successful synthesis of the product shown above (i.e., 3,3-dimethyl-2-butanol). [10]

CSE 2025 · Q3(a)(ii) Ketone A from isobutanol alone [5 marks]

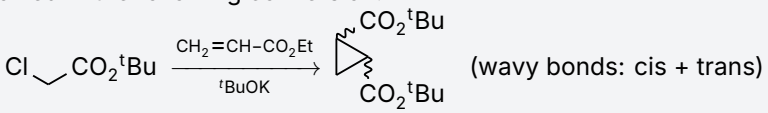
(ii) Describe the synthesis of ketone (*A*) when only isobutanol is available as the starting material:



A [5]

CSE 2025 · Q3(b) Cyclopropane from tert-butyl chloroacetate and ethyl acrylate; Structures of C and D [15 marks]

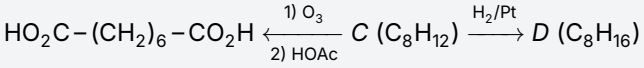
(i) Write the steps involved in the following conversion:



(wavy bonds: cis + trans)

[10]

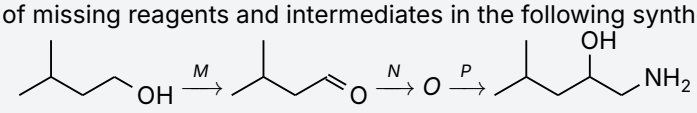
(ii) Elucidate the structure of *C* and *D* in the following conversion:



[5]

CSE 2025 · Q3(c)(i) Missing reagents and intermediate [10 marks]

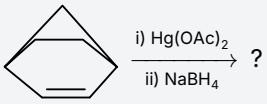
(i) Provide the structure of missing reagents and intermediates in the following synthesis:



[10]

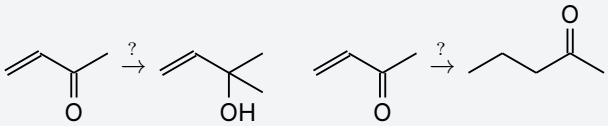
IFoS 2025 · Q1(e) Oxymercuration of norbornene [5 marks]

Write the products of the following reaction and justify the stereochemical outcome with an appropriate mechanism :



IFoS 2025 · Q4(c)(ii) 1,2 versus 1,4 addition [5 marks]

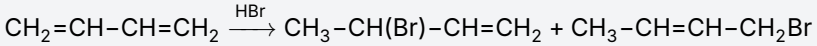
(ii) Complete the following reactions and give suitable explanation for the formation of the major products :



2024

CSE 2024 · Q2(a)(ii) 1,2- and 1,4-addition of HBr to butadiene [5 marks]

(ii) Consider the following reaction:



At −80 °C, 1,2-addition product predominates while at −45 °C, 1,4-addition product prefers. Justify. 5

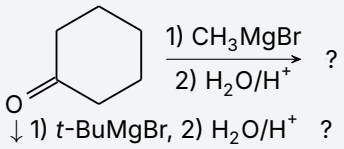
CSE 2024 · Q3(a) Methyl cyanide heated with dilute HCl; Bromine addition to cis- and trans-2-butene [15 marks]

(i) Predict the reaction mechanism and the major product formed when methyl cyanide is heated with dilute hydrochloric acid. 10

(ii) Addition of bromine to *cis*-2-butene gives racemic-2,3-dibromobutane while *trans*-2-butene yields *meso*-2,3-dibromobutane. Justify. 5

IFoS 2024 · Q4(a) Grignard addition and competing reduction [10 marks]

Complete the following reactions giving proper explanation for the formation of products with their spread :

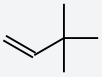


2023

CSE 2023 · Q4(a) Norbornene with D–Br; Relative rates of bromination in methanol; Hydroboration–oxidation of a tetrasubstituted alkene [20 marks]

(i)  $\xrightarrow[H_2O]{D-Br}$ (A) + (B)

Complete the above reaction and write the steps involved in the reaction. (5 marks)

(ii)  (A)  (B)  (C)  (D)

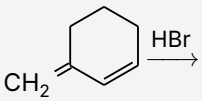
Arrange the above alkenes in ascending order of their relative rate of bromination in methanol. (5 marks)

(iii) $Ph_2C=C(C_2H_5)_2 \xrightarrow{BH_3 \cdot THF}$ (A) $\xrightarrow{H_2O_2, \ominus OH}$ (B)

Complete the above reactions and give suitable mechanism. (10 marks)

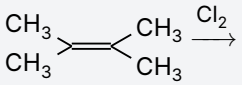
IFoS 2023 · Q3(a) Hydrogen bromide addition to a conjugated diene [5 marks]

Predict the product(s) of the following reaction. Which product will be major and why ?



IFoS 2023 · Q4(a) Two electrophilic additions with unusual outcomes [5 marks]

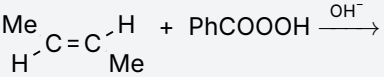
Complete the following reactions :

(i)  $\xrightarrow{Cl_2}$ (ii) $Ph-CH=C=CH_2 \xrightarrow{HCl/AcOH}$

2022

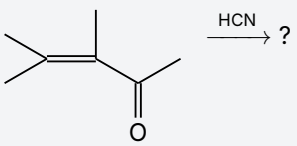
CSE 2022 · Q4(a)(i) trans-But-2-ene with perbenzoic acid, then hydroxide [10 marks]

(i) Complete the following reaction by showing stepwise reaction mechanism for the formation of products:

 + PhCOOOH $\xrightarrow{OH^-}$ 10

IFoS 2022 · Q1(b) Cyanide addition to a hindered enone [5 marks]

Invoking the idea of kinetic and thermodynamic control, write the products (major and minor) in the following reaction:



2021

CSE 2021 · Q1(d) Two aldehydes towards a nucleophile in the presence of $BF_3 \cdot OEt_2$ [10 marks]

Discuss the reactivity of following compounds towards nucleophile in the presence of $BF_3 : OEt_2$:

(i) *p*-trifluoromethyl benzaldehyde (ii) *p*-tolualdehyde

CSE 2021 · Q4(b) 3,3-Dimethylbut-1-ene with HCl; Allyl bromide with HBr, without and with benzoyl peroxide [15 marks]

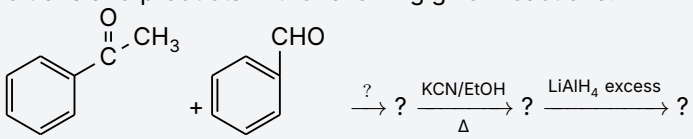
(i) $(CH_3)_3C-CH=CH_2 \xrightarrow{HCl} ?$ 5

(ii) $CH_2=CH-CH_2-Br \xrightarrow{HBr} ? \xrightarrow[\text{benzoyl peroxide}]{HBr} ? \xrightarrow[\text{benzoyl peroxide}]{HBr} ?$ 10

Write the product(s) of the above reactions.

IFoS 2021 · Q2(d)(ii) Chalcone, cyanide addition and reduction [5 marks]

(ii) Write the reaction conditions and products in the following given reactions: 5



IFoS 2021 · Q4(d)(i) Regioselective hydration of allylbenzene [5 marks]

(i) Write the reagents of the following conversions and give appropriate mechanism: 5

$Ph-CH_2-CH=CH_2 \xrightarrow{A} Ph-CH_2-CH(OH)-CH_3$; $Ph-CH_2-CH=CH_2 \xrightarrow{B} Ph-CH_2-CH_2-CH_2-OH$

IFoS 2021 · Q7(a)(ii) Hydration followed by oxidation [5 marks]

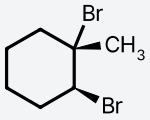
(ii) Complete the following reaction sequence and give suitable mechanism: 5

$$(CH_3)_2CH-CH=CH_2 \xrightarrow{\text{(i) } Hg(OAc)_2} A \xrightarrow{NaBH_4} B \xrightarrow[H^+]{CrO_3} C$$

2020

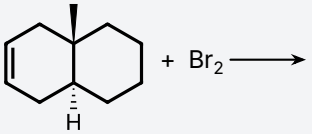
CSE 2020 · Q1(c) trans-1,2-Dibromo-1-methylcyclohexane from methylcyclohexane [10 marks]

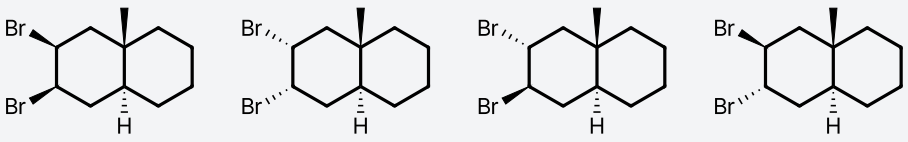
Starting with methylcyclohexane, how could you prepare the following vicinal *trans*-dihalide?



CSE 2020 · Q3(c) Bromination of an octalin; DBr and 1,3-cyclohexadiene [20 marks]

(i) Identify the kinetically favoured product from the reaction given below. Justify your choice of the product:





A *B* *C* *D*

(ii) Write the kinetic as well as thermodynamic product(s) of the reaction of DBr with 1,3-cyclohexadiene. Which product (kinetic or thermodynamic) would be formed more readily at higher temperature? Identify the

more stable product and justify your choice of the more stable product.

CSE 2020 · Q4(b) Rates of HCl addition: an enol ether reacts fastest [15 marks]

Consider the following reactions *X*, *Y* and *Z*, and answer the given questions:

X: propene + HCl → 2-chloropropane + 1-chloropropane

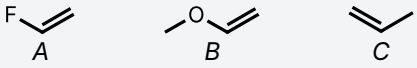
Y: 2-methoxypropene + HCl → 2-chloro-2-methoxypropane + 1-chloro-2-methoxypropane

Z: 3,3-dimethylbut-1-ene + HCl → 2-chloro-3,3-dimethylbutane + 1-chloro-3,3-dimethylbutane

(i) Which reaction is the fastest? Briefly explain.
(ii) What is the major product of the fastest reaction? Explain briefly.
(iii) Write a detailed curved arrow mechanism of the fastest identified reaction and identify the rate-determining step of your mechanism.
(iv) Offer an explanation for your choice of rate-determining step.

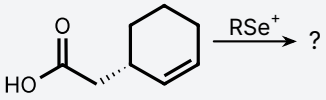
IFoS 2020 · Q1(e) Electrophilic addition: vinyl fluoride, methyl vinyl ether, propene [5 marks]

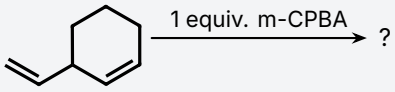
Out of *A*, *B* and *C*, identify the one that would react the fastest and the one that would react the slowest in a typical electrophilic addition reaction. Briefly explain your choice.



IFoS 2020 · Q3(a) Selenolactonisation; selective epoxidation of 4-vinylcyclohexene [10 marks]

Outlining the mechanism involved, write the product(s) of each of the following reactions and offer a suitable explanation for the choice of your product(s).

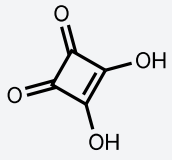
(i) 

(ii) 

2018

CSE 2018 · Q1(c) Squaric acid; acylation of trans-2-butene [10 marks]

(i) Account for the fact that compound *A* is almost as strong an acid as H_2SO_4 :

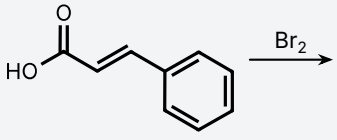


A

(ii) What happens when *trans*-2-butene is reacted with CH_3COCl in presence of anhydrous $AlCl_3$?

IFoS 2018 · Q1(c) Bromination of trans-cinnamic acid: stereochemistry [5 marks]

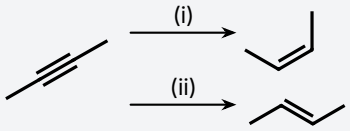
Write the structure of the product(s) with proper stereochemical outcome of the following reaction and also the corresponding mechanistic pathway:



2017

CSE 2017 · Q4(e) But-2-yne to cis- and trans-but-2-ene [10 marks]

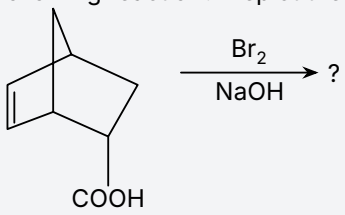
Write specific reagents necessary for each of the following transformations. Out of 'stereospecific' and 'stereoselective', which one suits for each reaction?



2016

IFoS 2016 · Q2(c)(i) Bromolactonisation of endo-norbornene-carboxylic acid [5 marks]

What product can one expect from the following reaction? Depict the stereochemical outcome at every step.



IFoS 2016 · Q2(c)(ii) Octalin to the tertiary and the secondary decalol [5 marks]

What reagents are needed to bring the transformation?

