II.3 Reactive Intermediates

Civil Services 2016–2026: **19** parts, **190** marks · IFoS 2016–2025: **23** parts, **135** marks

Syllabus. Generation, geometry, stability and reactions of carbonium ions and carbanions, free radicals, carbenes, benzynes and nitrenes.

Marks	2016	2017	2018	2019	2020	2021	2022	2023	2024	2025	2026
CSE	25	10	0	10	25	20	20	15	20	25	20
IFoS	5	35	5	5	10	10	25	15	20	5	

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.

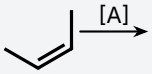
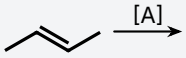
2026

CSE 2026 · Q2(c) Dichlorocarbene and its reactions [20 marks]

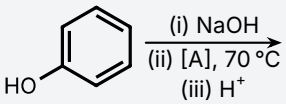
Intermediate [A] is formed in the following reaction: $CHCl_3 + {}^tBuOK \longrightarrow [A]$

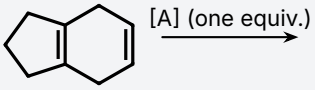
(i) Identify the intermediate [A].

(ii) Write the products of the following reactions with the correct stereochemistry.

Reaction 1  Reaction 2 

(iii) Are reactions 1 and 2 stereospecific or stereoselective?

(iv) Write the structure of the major product formed in the following reaction: 

(v) Write the major product formed in the following reaction: 

2025

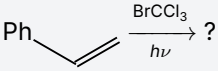
CSE 2025 · Q1(d) Spin state of a carbene; p-bromophenol with $NaNH_2$ [10 marks]

(i) Discuss in detail how the reaction of a carbene with *cis*-2-butene can be used to define the spin state (S/T) of carbene.

(ii) *para*-Bromophenol on reaction with $NaNH_2/NH_3$ (*l*) followed by acidic workup yields one major product. Explain the reaction by writing the steps involved.

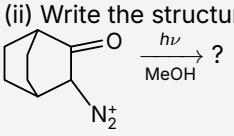
CSE 2025 · Q2(b)(ii) Styrene with $BrCCl_3$ under light [5 marks]

(ii) Write the structure of the major product(s) formed in the following reaction. Justify your answer:

 [5]

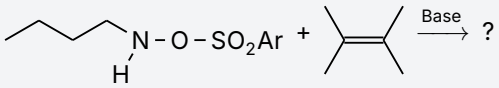
CSE 2025 · Q3(c)(ii) Photolysis of the α-diazoketone in methanol [10 marks]

(ii) Write the structure of the product formed and the steps involved in the following reaction:

 [10]

IFoS 2025 · Q1(b) Nitrene transfer to an alkene [5 marks]

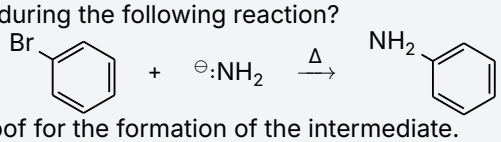
Write the major product of the following reaction and give mechanism :



2024

CSE 2024 · Q1(b) Intermediate in the amination of bromobenzene [10 marks]

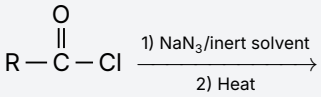
What is the intermediate formed during the following reaction?



Explain any one experimental proof for the formation of the intermediate.

CSE 2024 · Q3(c)(i) Acyl chloride to isocyanate; singlet and triplet nitrene [10 marks]

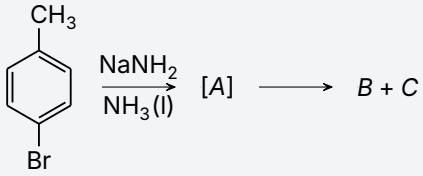
(i) Consider the following conversion:



Show that the above conversion involves the formation of nitrene intermediate. Draw the orbital pictures of singlet and triplet states of nitrene. 10

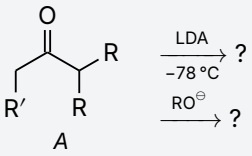
IFoS 2024 · Q1(d) Amination through a benzyne [5 marks]

Predict the products [*A*], *B* and *C*. Also give the reaction mechanism of the following reaction sequence :



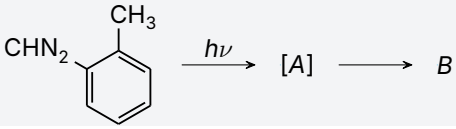
IFoS 2024 · Q2(a)(ii) Kinetic and thermodynamic enolates [5 marks]

(ii) Predict the generation of reactive chemical species giving suitable explanation in terms of thermodynamic/kinetic control in the following chemical equations :



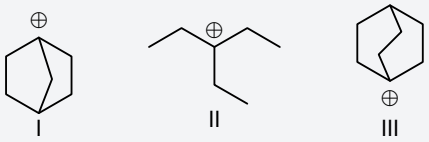
IFoS 2024 · Q2(b)(i) Photolysis of an ortho-methyl diazo compound [5 marks]

(i) Identify the products [*A*] and *B* in the following reaction :



IFoS 2024 · Q2(b)(ii) Bridgehead carbocation stability [5 marks]

(ii) Arrange the following chemical entities in order of their decreasing stability :



2023

CSE 2023 · Q1(b)(ii) Dimerisation ability of three triarylmethyl-type radicals [5 marks]

(ii) $Ph_3C^{\bullet}$ (A) $(p\text{-}FC_6H_4)_3C^{\bullet}$ (B) $Ph_2(t\text{-}Bu)C^{\bullet}$ (C)

Arrange the above radicals in ascending order of their dimerisation ability. (5 marks)

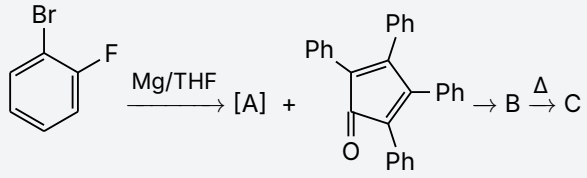
CSE 2023 · Q2(b)(iii) Ketene, hv, then cis-but-2-ene [10 marks]

(iii) $H_2C{=}C{=}O \xrightarrow[\text{ii) } cis\text{-but-2-ene}]{\text{i) } h\nu} ?$

Write the major product of the above reaction showing proper stereochemistry and explain the mechanism. (10 marks)

IFoS 2023 · Q1(c) Benzyne capture by tetracyclone [5 marks]

Complete the following reaction and identify the products A, B and C.

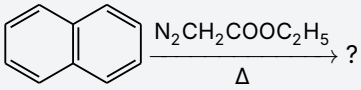


IFoS 2023 · Q3(c) Solvolysis and antiaromatic destabilization [5 marks]

Compare the rate of solvolysis in separate reactions of (i) iodocyclopentane and (ii) 1-iodo-2,4-cyclopentadiene with silver perchlorate in propionic acid.

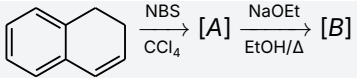
IFoS 2023 · Q4(f) Buchner ring expansion [5 marks]

Predict the product(s) of the following reaction :



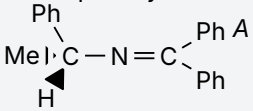
2022

CSE 2022 · Q2(b)(ii) 1,2-Dihydronaphthalene with NBS, then sodium ethoxide [5 marks]

(ii) Predict [*A*] and [*B*] in the following reaction: 

5

CSE 2022 · Q4(a)(ii) Loss of optical activity of an imine with sodium ethoxide [5 marks]

(ii) The compound *A* is optically active and upon treating *A* with alcoholic sodium ethoxide, it looses its optical activity. Justify: 

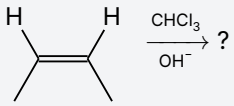
A 5

CSE 2022 · Q4(b)(i) Dibromocyclopentanes from cyclopentane and excess bromine [10 marks]

(i) If more than one equivalent of Br_2 at high temperature are allowed to react with cyclopentane, how many dibromocyclopentanes would you expect as products? Draw their structures and name them. 10

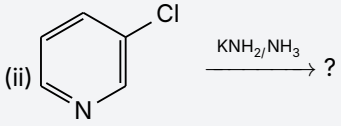
IFoS 2022 · Q1(d) Dichlorocarbene trapping [5 marks]

Giving the mechanism, write the product(s) of the following reaction. Prove the formation of intermediate involved in the reaction using a suitable trap:



IFoS 2022 · Q3(a)(ii) Amination through 3,4-pyridyne [10 marks]

Complete the following reactions with their mechanisms:



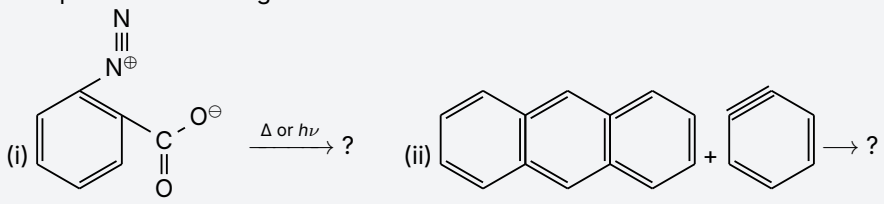
IFoS 2022 · Q3(e) Stability of three carbanions [5 marks]

Arrange the following according to their stability with proper justification:

$R_3C-CH_2^{\ominus}$, $R_2C=CH^{\ominus}$, $R-C\equiv C^{\ominus}$

IFoS 2022 · Q4(d) Benzyne generation and capture [5 marks]

Complete the following reactions:

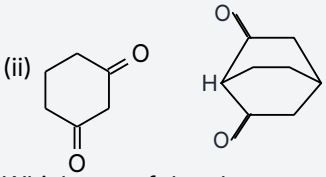


2021

CSE 2021 · Q2(b) Cyclopropylmethyl cation; acidity of two 1,3-diones; a diazo ester heated in cyclohexane [15 marks]

(i) Comment upon the structure and stability of cyclopropylmethyl carbocation.

(ii)



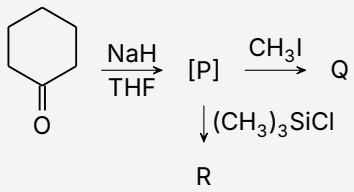
Which one of the above compound is more acidic and why?

(iii)  + $Me_3C-O-C(=O)-CHN_2 \xrightarrow{\Delta}$

Write the product(s) in the above reaction.

CSE 2021 · Q2(c)(ii) Cyclohexanone enolate with methyl iodide and with trimethylsilyl chloride [5 marks]

(ii)



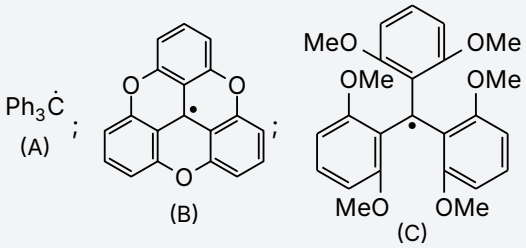
Write down the products in the above reactions. 5

IFoS 2021 · Q7(c)(ii) Ring expansion of vinylcyclobutane [5 marks]

(ii) What will happen when vinyl cyclobutane reacts with methanol in presence of catalytic amount of H_2SO_4? Give the product with reaction mechanism. 5

IFoS 2021 · Q7(d) Stability of triarylmethyl radicals [5 marks]

Arrange the following free radicals in order of their stability with proper justification:



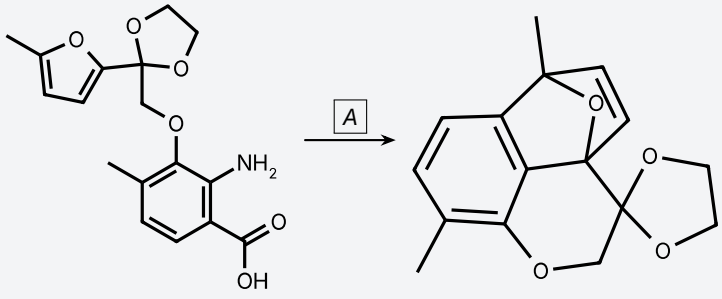
2020

CSE 2020 · Q1(b) Carbonium ion and carbocation [10 marks]

Define carbonium ion. Is it identical or different with respect to carbocation? Explain giving suitable examples.

CSE 2020 · Q3(b) Benzyne from an anthranilic acid, trapped by a tethered furan [15 marks]

Mention the reagent(s) and write the mechanism for the following conversion:



IFoS 2020 · Q1(f) Red trityl radical from Ph_3CCl and Zn; bleaching by oxygen [5 marks]

A red colour is formed on reaction of Ph_3CCl with Zn in benzene and it disappears on passing oxygen in the reaction mixture. Account for the observations.

IFoS 2020 · Q3(c) Hex-5-enyl radical cyclisation with Bu_3SnH [5 marks]

Hex-5-enyl bromide on reaction with BuSnH at 60 °C produces a mixture of products. Write the structure of each product, mention the highest yielding product and account for its formation.

2019

CSE 2019 · Q1(b) One benzyne from two dichlorobenzenes [10 marks]

1,2-dichlorobenzene and 1,3-dichlorobenzene upon treatment with KNH_2 give same product. Account for this.

IFoS 2019 · Q1(d) Planar $\cdot CH_3$ but pyramidal $\cdot CF_3$ [5 marks]

Methyl radical ($\dot{C}H_3$) is planar, while trifluoromethyl radical ($\dot{C}F_3$) is pyramidal. Justify.

2018

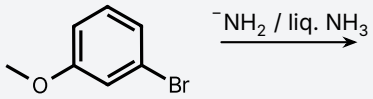
IFoS 2018 · Q2(e) 3-Bromoanisole with NH_2^- /liquid NH_3: benzyne [5 marks]

Account for the formation of product(s) from a reaction of 3-bromoanisole with $\bar{N}H_2$/liq. NH_3.

2017

CSE 2017 · Q4(b) 3-Bromoanisole and amide ion: benzyne regiochemistry [10 marks]

Predict the product(s) with mechanism and justify your answer.



IFoS 2017 · Q1(h) Why di-t-butoxycarbene is unreactive [5 marks]

Explain why di-*t*-butoxycarbene is unreactive.

IFoS 2017 · Q3(a) Stability order of methyl, ethyl, isopropyl and t-butyl radicals [10 marks]

Write down the stability order of the following alkyl radicals. Explain your answer.

$\dot{C}H_3$, $MeCH_2$, Me_2CH and Me_3C

IFoS 2017 · Q3(d) cis-2-Butene with singlet and triplet carbene [10 marks]

Cis-2-butene + Singlet carbene ⟶ ?

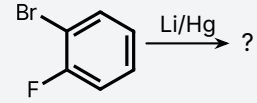
Cis-2-butene + Triplet carbene ⟶ ?

Mention the product(s) in each of the above cases. Substantiate your answer.

IFoS 2017 · Q4(c) [14]- vs [16]annulene; nitrene and benzyne products [10 marks]

(i) Between [14] Annulene and [16] Annulene – which one is aromatic and why? 5

(ii) Write the structure of the product formed in the following reactions:

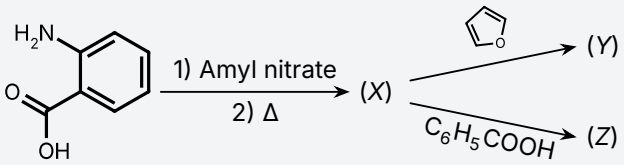
1. $H-\ddot{N}: + CH_2=CH_2 \longrightarrow$?
2. 

? 5

2016

CSE 2016 · Q2(b) Benzyne from anthranilic acid; trapping with furan and benzoic acid [15 marks]

Identify the intermediate (*X*) and the products (*Y*) and (*Z*) in the given reaction:

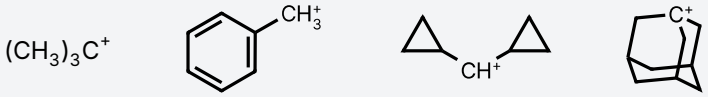


CSE 2016 · Q2(c) Singlet and triplet carbenes with cis-pent-2-ene [10 marks]

Discuss the stereospecificity of addition of singlet and triplet carbenes to *cis*-2-pentene.

IFoS 2016 · Q1(d) Order of carbocation stability [5 marks]

Arrange the following carbocations in decreasing order of their stability. Give reason in support of your answer.



A B C D