II.11 Synthetic Uses of Reagents

Civil Services 2016–2026: **47** parts, **530** marks · IFoS 2016–2025: **33** parts, **225** marks

Syllabus. OsO_4, HIO_4, CrO_3, $Pb(OAc)_4$, SeO_2, NBS, B_2H_6, Na-liquid NH_3, $LiAlH_4$, $NaBH_4$, n-BuLi, MCPBA.

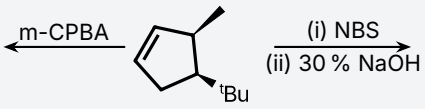
Marks	2016	2017	2018	2019	2020	2021	2022	2023	2024	2025	2026
CSE	65	45	85	50	45	45	45	40	45	25	40
IFoS	10	5	65	10	35	15	20	25	25	15	

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

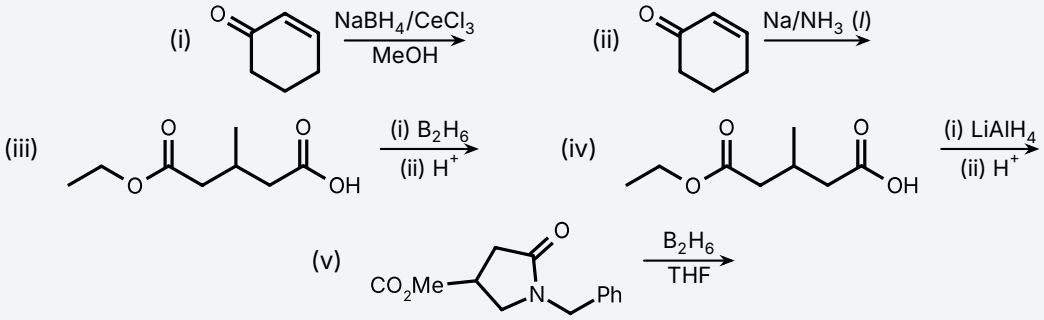
CSE 2026 · Q5(b) Two epoxides of opposite face from one cyclopentene [10 marks]

Write the structure of the major product indicating the stereochemistry and mechanism of the following reactions:



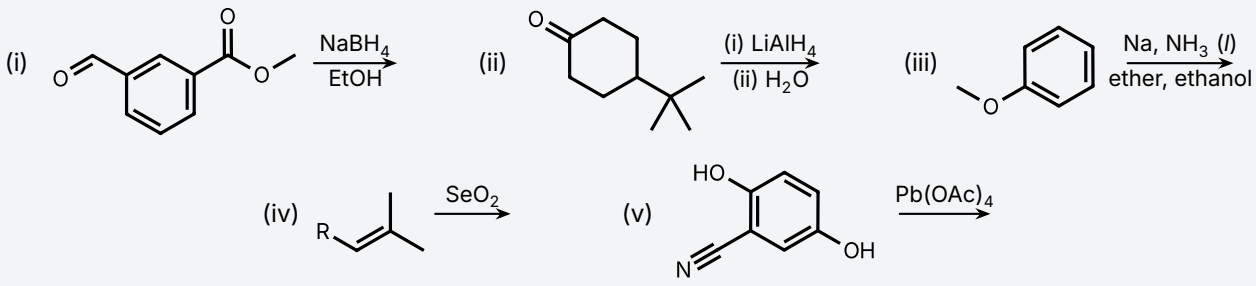
CSE 2026 · Q6(a) Chemoselective reductions [10 marks]

Write the structures of the products formed in the following reactions:



CSE 2026 · Q7(c) Reagents: $NaBH_4$, $LiAlH_4$, Birch, SeO_2, $Pb(OAc)_4$ [20 marks]

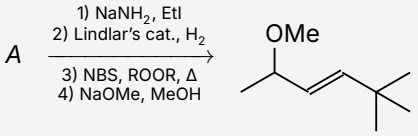
Write the structure of the major product formed in the following reactions and provide the mechanism:



2025

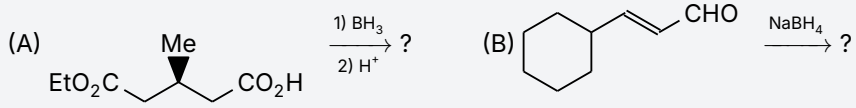
CSE 2025 · Q5(b) Starting material A and the intermediates [10 marks]

Deduce the structure of the starting material (*A*) and all the intermediates formed in each step that would lead to the formation of the following product through the defined reactions:



CSE 2025 · Q6(a) Products and intermediates of two reductions; Role of NMO in catalytic dihydroxylation [15 marks]

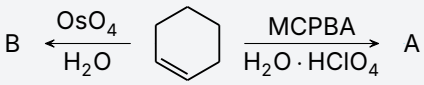
(i) Elucidate the structure of the product and the intermediate (if any) in the following reactions: 5+5=10



(ii) Describe the role of NMO during the dihydroxylation of an alkene using catalytic amount of OsO_4 in the presence of N-methylmorpholine N-oxide (NMO). 5

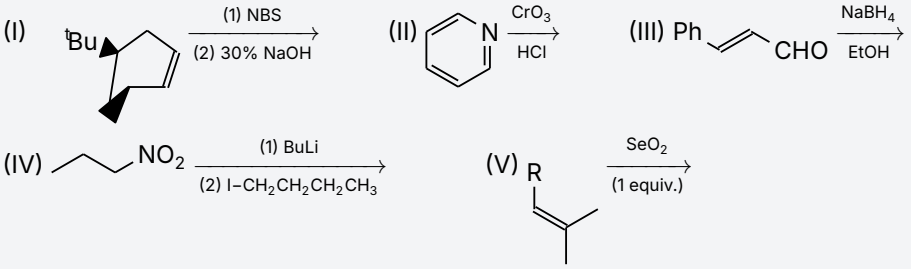
IFoS 2025 · Q6(c)(ii) Syn and anti dihydroxylation [5 marks]

(ii) Mention the product of the given reactions with proper mechanism: 5



IFoS 2025 · Q7(c) Five reagent-based transformations [10 marks]

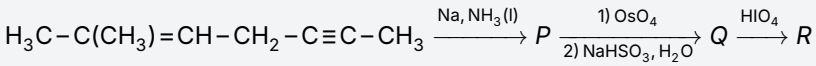
Write down the major product of the following reactions:



2024

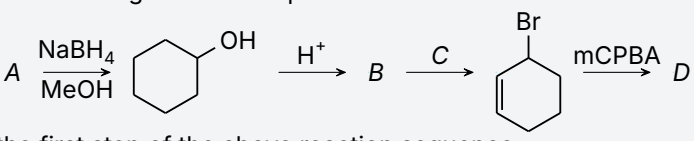
CSE 2024 · Q5(b) P, Q and R from an enyne [10 marks]

Predict the structure of *P*, *Q* and *R* in the following sequence of reactions:



CSE 2024 · Q6(c) A, B, C and D; mechanism of the $NaBH_4$ step [20 marks]

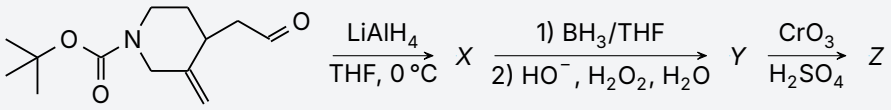
Identify *A*, *B*, *C* and *D* in the following reaction sequence:



Write the mechanism of the first step of the above reaction sequence.

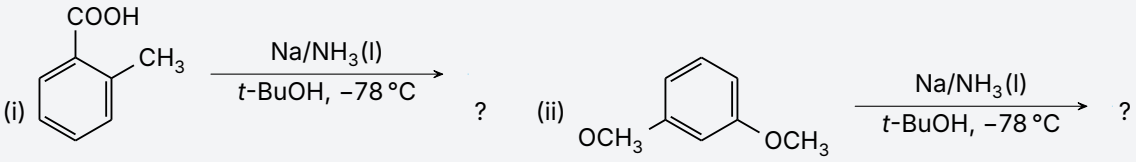
CSE 2024 · Q7(b) X, Y and Z from an N-Boc piperidine aldehyde [15 marks]

Predict the structure of *X*, *Y* and *Z* in the following sequence of reactions:



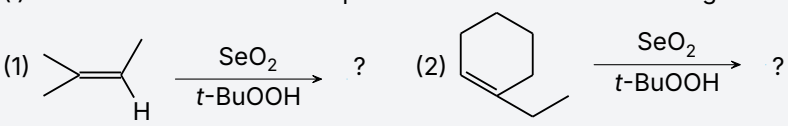
IFoS 2024 · Q5(c) Two Birch reductions [5 marks]

Complete the following reactions:

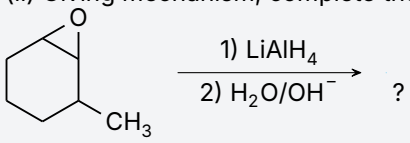


IFoS 2024 · Q6(a) Selenium dioxide allylic oxidation; Reductive opening of a cyclic epoxide [10 marks]

(i) Write the structures of the products formed in the following reactions: 5

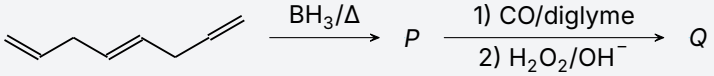


(ii) Giving mechanism, complete the following reaction: 5

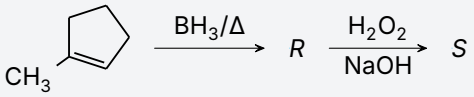


IFoS 2024 · Q7(a) Hydroboration followed by carbonylation; Thermal organoborane isomerization [10 marks]

Write the structures of the products in the following reaction sequences:

(i) 

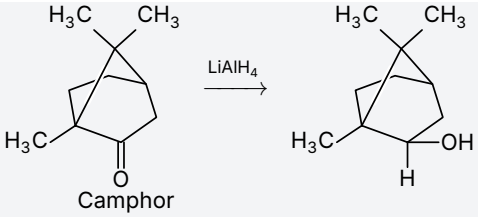
5

(ii) 

5

2023

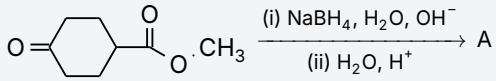
CSE 2023 · Q5(d) $LiAlH_4$ reduction of camphor: OH cis to the bridge [10 marks]

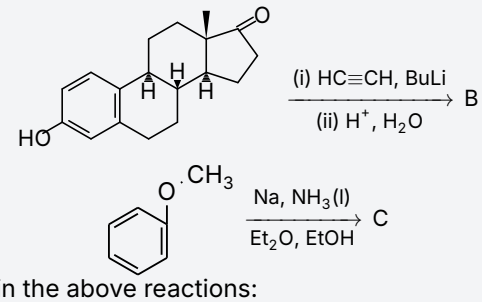


Reduction of camphor with $LiAlH_4$ leads to 90% of the isomer in which the OH group is cis to the bridge. Give a suitable explanation of this observation.

CSE 2023 · Q6(b)(i) Products A, B and C [10 marks]

(i)

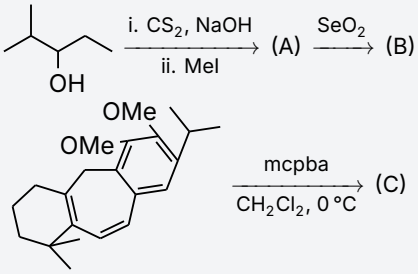


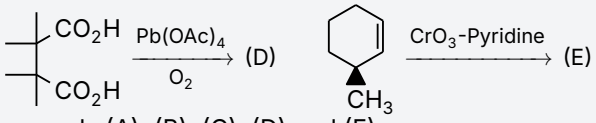


Write the structure of product(s) in the above reactions: *10*

CSE 2023 · Q7(c) Structures of (A), (B), (C), (D) and (E); Osmate ester from cyclohexene; oxidation state and geometry of osmium; D-Mannitol: cyclohexylidene ketal, then HIO_4 [20 marks]

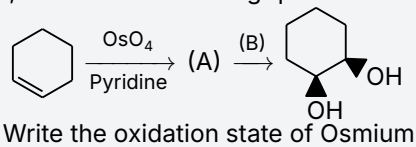
(i)





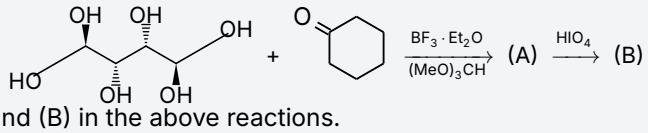
Write the structure of the compounds (A), (B), (C), (D) and (E). *10*

(ii) From the reaction sequence below, answer the following questions:



(I) Write structure of (A) and (B) (II) Write the oxidation state of Osmium in the intermediate (A) and its geometry. *5*

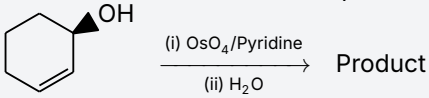
(iii)



Write the structure of (A) and (B) in the above reactions. *5*

IFoS 2023 · Q5(b) Osmium dihydroxylation of an allylic alcohol [5 marks]

Write the product for the following reaction and offer a suitable explanation for your answer.

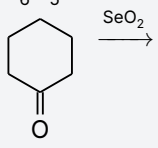


IFoS 2023 · Q6(a) Selective reduction and alpha oxidation [10 marks]

Complete the following reactions and give their mechanism:

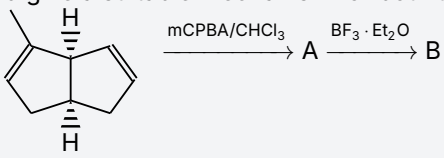
(i) $C_6H_5-CH=CH-CHO + LiAlH_4 \xrightarrow{Et_2O/RT}$

(ii)



IFoS 2023 · Q8(a) Selective epoxidation and carbonyl rearrangement [10 marks]

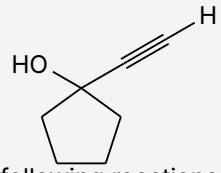
Complete the following reactions and give a suitable mechanism for both the steps:



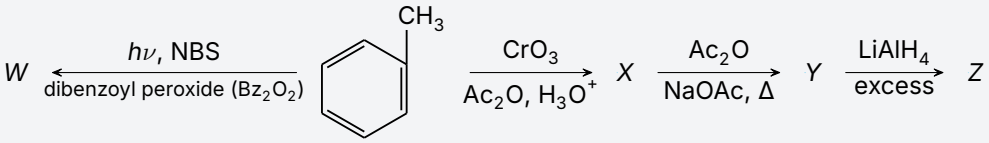
2022

CSE 2022 · Q5(c) 1-Ethynylcyclopentanol from acetylene; Products W, X, Y and Z from toluene [10 marks]

(i) By using appropriate reactants, reagents and conditions and using acetylene as starting material, how will you synthesize the following compound?

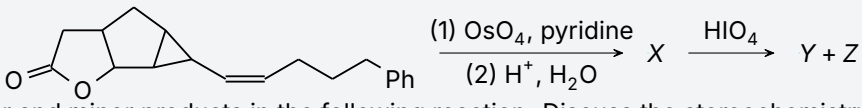


(ii) Identify the products *W*, *X*, *Y* and *Z* in the following reactions:

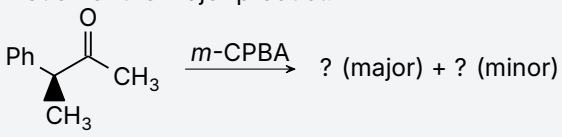


CSE 2022 · Q6(c) OsO_4, then HIO_4, on an alkenyl cyclopropane lactone; (S)-3-Phenylbutan-2-one with m-CPBA [20 marks]

(i) Write the structures of the products *X*, *Y* and *Z* in the following reactions and indicate the mechanism for the formation of *X*:



(ii) Write the major and minor products in the following reaction. Discuss the stereochemistry along with reaction mechanism for the formation of the major product:



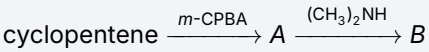
CSE 2022 · Q7(b) Butanoyl chloride with 2 $NaBH_4$, then H_3O^+; But-2-yne with sodium in liquid ammonia [15 marks]

Complete the following reactions and give suitable mechanisms for the formation of products:

(i) $CH_3-CH_2-CH_2-COCl \xrightarrow[(2)\ H_3O^+]{(1)\ 2NaBH_4} ?$ (ii) $CH_3-C\equiv C-CH_3 \xrightarrow{Na \text{ in liq. } NH_3} ?$

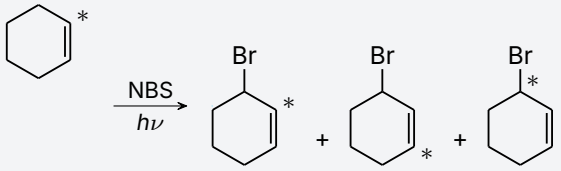
IFoS 2022 · Q5(g) Epoxide opening by dimethylamine [5 marks]

Write the products of the following reaction and predict the mechanism:



IFoS 2022 · Q5(h) Labelled allylic bromination [5 marks]

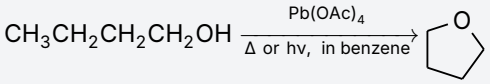
How will you account for the formation of the following products on treatment of labelled (∗ = ^{14}C) *A* with NBS?



A

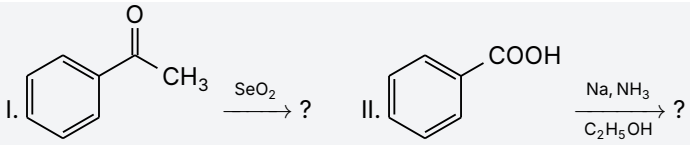
IFoS 2022 · Q7(e) Lead tetraacetate cyclization of butanol [10 marks]

Propose the mechanism for the following reaction:



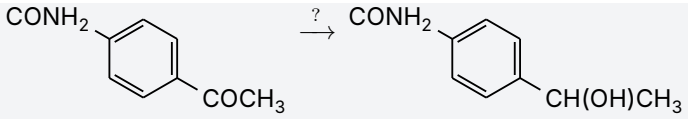
2021

CSE 2021 · Q5(c) Acetophenone with SeO_2; benzoic acid with Na in liquid NH_3 [10 marks]



Predict the product(s) and suggest mechanism in each of the above chemical transformations.

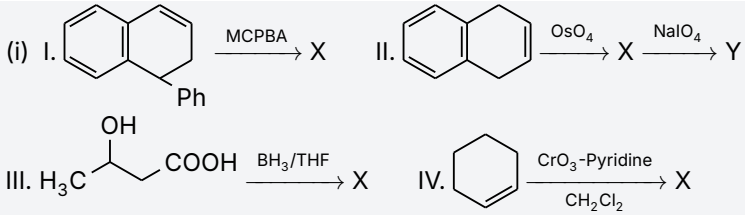
CSE 2021 · Q7(b) $LiAlH_4$ and $NaBH_4$: solvents, reactivity and choice of reagent [15 marks]



$CH_3-CH(OH)-C\equiv C-CH_3 \xrightarrow{?} CH_3-CH(OH)-CH=CH-CH_3$ (*E*, H atoms trans)

Discuss the solvent compatibility for $LiAlH_4$ and $NaBH_4$ reagents and the factors responsible for differential reactivity. Also suggest preferred reagent between the two for the above transformations.

CSE 2021 · Q8(a) Products X and Y in four reagent problems; 2-Methylbut-1-ene with diborane [20 marks]

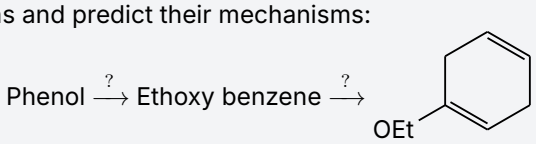


Write the products X/Y in the above chemical transformations.

(ii) Predict the product in the reaction of 2-methyl-1-butene with diborane. Account for the regioselectivity observed in the reaction.

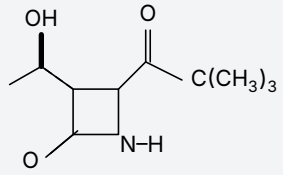
IFoS 2021 · Q1(f) Phenol to a reduced aryl ether [5 marks]

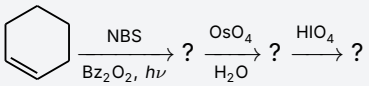
Complete the following reactions and predict their mechanisms:



IFoS 2021 · Q4(b) Oxidation and oxidative cleavage [5 marks]

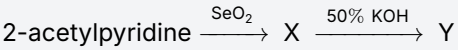
Complete the following reactions:

(i) 

(ii) 

IFoS 2021 · Q5(d) Oxidation of 2-acetylpyridine [5 marks]

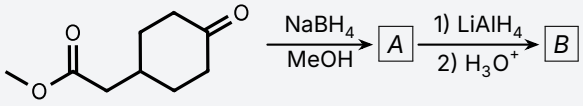
Identify the products X and Y in the following reactions and propose suitable mechanism for their formation:



2020

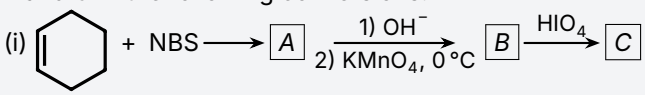
CSE 2020 · Q5(b) Chemoselective reduction: $NaBH_4$ then $LiAlH_4$ [10 marks]

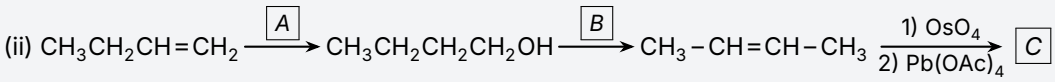
Identify the compounds *A* and *B* in the following reaction sequence:



CSE 2020 · Q6(c) NBS, $KMnO_4$, HIO_4; hydroboration, dehydration, OsO_4 and $Pb(OAc)_4$ [20 marks]

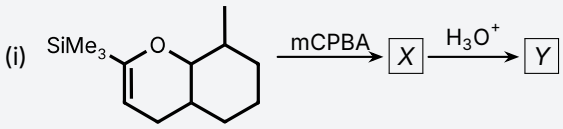
Identify the compounds *A*, *B* and *C* in the following conversions:

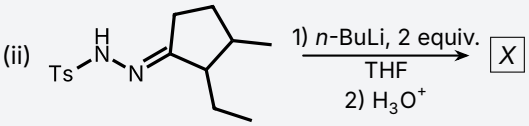
(i) 

(ii) 

CSE 2020 · Q8(b) Epoxidation of a silyl dihydropyran; the Shapiro reaction [15 marks]

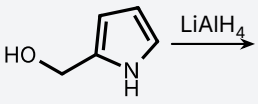
Identify *X* and *Y* in the following reactions and outline the mechanism for the formation of *X* in both the reactions:

(i) 

(ii) 

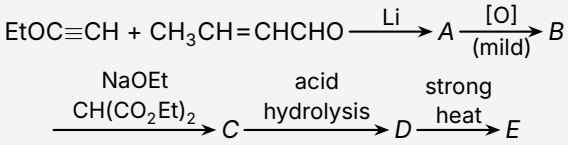
IFoS 2020 · Q1(c) $LiAlH_4$ on pyrrole-2-methanol [5 marks]

Predict the product of the following reaction and write the mechanism.



IFoS 2020 · Q2(d) Ethoxyacetylene with crotonaldehyde, then malonate sequence (A–E) [10 marks]

Write the structure of the products (*A* – *E*) in the following set of reactions:

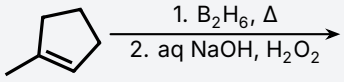


IFoS 2020 · Q5(b) Cyclohexanone to cyclohexane-1,2-dione [5 marks]

How can cyclohexane-1,2-dione be obtained from cyclohexanone? Give its mechanism.

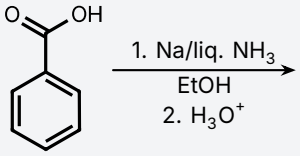
IFoS 2020 · Q5(c) Hydroboration and isomerisation of 1-ethylidene-type cyclopentene [5 marks]

Write the structure of the intermediate and also the final product showing relative stereochemistry of the ring attached groups in each, and write the mechanism of the second step.

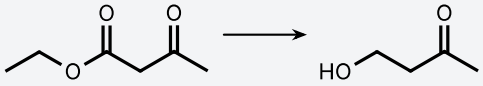


IFoS 2020 · Q7(d) Birch reduction of benzoic acid; chemoselective reduction of a keto ester [10 marks]

(i) Write the structure of the product with mechanism, and account for its formation in the following reaction:



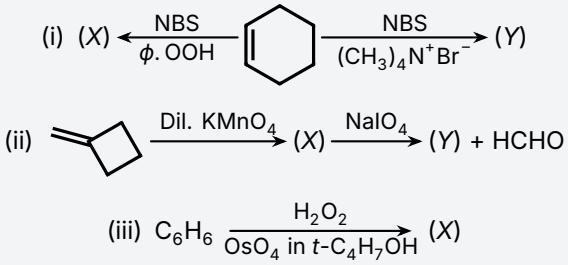
(ii) Carry out the following transformation:



2019

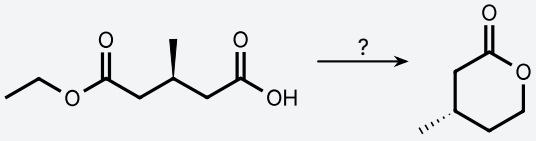
CSE 2019 · Q6(b) NBS (radical and ionic), $KMnO_4/NaIO_4$, OsO_4/H_2O_2 [15 marks]

Identify (*X*) and (*Y*) in the following:



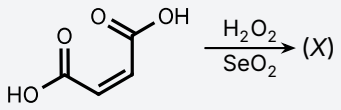
CSE 2019 · Q7(b) Borane: acid reduced, ester kept; δ-lactone [15 marks]

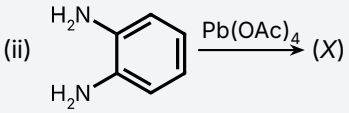
Name the reagent for the following regioselective conversion. Propose the mechanism:

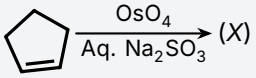


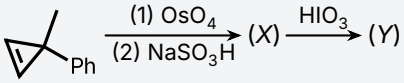
CSE 2019 · Q7(c) SeO_2/H_2O_2, $Pb(OAc)_4$, OsO_4, periodate [20 marks]

Write the products (*X*) and (*Y*) of the following reactions:

(i) 

(ii) 

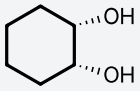
(iii) 

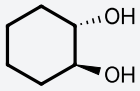
(iv) 

Comment on the stereochemistry of product (*X*) in each case.

IFoS 2019 · Q5(g) trans- and cis-cyclohexane-1,2-diol from cyclohexene [5 marks]

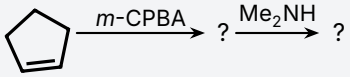
How do you prepare the following compounds from cyclohexene? Explain the stereochemistry during their formation:

(i) 

(ii) 

IFoS 2019 · Q5(h) Epoxidation of cyclohexene then ring-opening by Me_2NH [5 marks]

Complete the following reaction and predict the mechanism:



2018

CSE 2018 · Q1(b) NBS: preparation and allylic bromination of propene [10 marks]

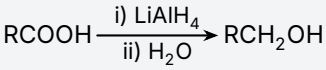
How is NBS obtained from succinimide? Write its reaction with propene in presence of sunlight. Outline the mechanism.

CSE 2018 · Q2(a) Hydroboration–oxidation of 1-methylcyclopentene [10 marks]

By taking 1-methylcyclopentene as an example, explain hydroboration-oxidation reaction. Justify that it is stereoselective and regioselective.

CSE 2018 · Q2(c) Reduction of a carboxylic acid by $LiAlH_4$; chemoselectivity of $NaBH_4$ [15 marks]

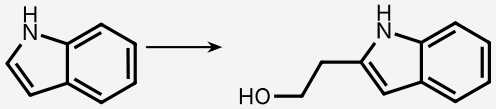
Outline the mechanism for the following reaction :

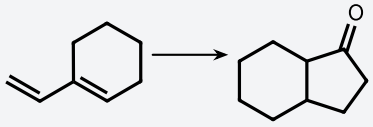


In what way is $NaBH_4$ different from $LiAlH_4$ in 'chemoselectivity'?

CSE 2018 · Q3(a) Two transformations: indole and 1-vinylcyclohexene [10 marks]

Carry out the following transformations :

(i) 

(ii) 

CSE 2018 · Q6(a) Hydroxyl-directed epoxidation: mCPBA versus V(acac)$_2$/TBHP [15 marks]

When *trans*-4-*tert*-butylcyclohex-2-enol is reacted separately with mCPBA and V(acac)$_2$/*tert*-butylhydroperoxide, in the second reaction only one product is formed, whereas in the first case a mixture of two isomeric products is obtained. Write the structure of the product in each case with proper stereochemical outcome and justification.

CSE 2018 · Q7(b) OsO_4/pyridine hydroxylation of maleic and fumaric acids [10 marks]

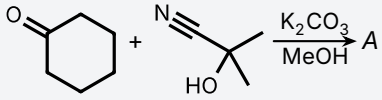
Write the structures of the products expected from hydroxylation of maleic acid and fumaric acid using OsO_4/Py, with the stereochemistry. What is the role of pyridine in the above reaction?

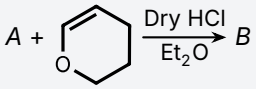
CSE 2018 · Q7(c) Birch reduction: mechanism and regiochemistry [15 marks]

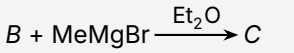
What is Birch reduction? Suggest its mechanism by taking a suitable example. Why does Birch reduction on benzene derivatives with an electron-donating group happen on *ortho* and *meta* positions?

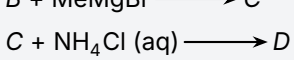
IFoS 2018 · Q3(c) Acetone cyanohydrin, THP protection and Grignard sequence (A–E) [10 marks]

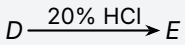
Write the structures (*A* to *E*) for the following sequence of reactions:





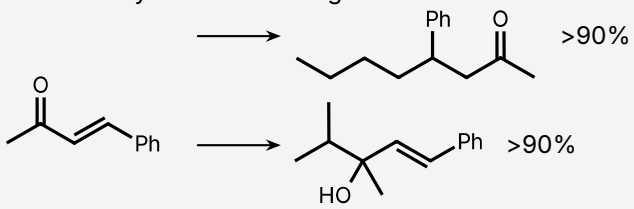






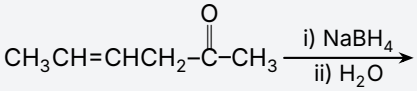
IFoS 2018 · Q3(d) 1,4- versus 1,2-addition to benzalacetone [10 marks]

Write the appropriate reagent necessary for the following two conversions and account for their formation:



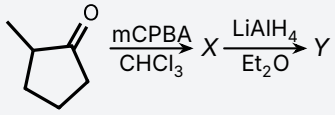
IFoS 2018 · Q5(g) $NaBH_4$ reduction of hex-4-en-2-one [5 marks]

Give the product of the following reaction:



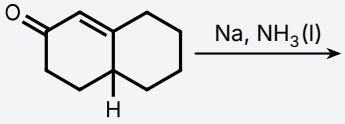
IFoS 2018 · Q6(c) Baeyer–Villiger then $LiAlH_4$ of 2-methylcyclopentanone [5 marks]

Identify the compounds *X* and *Y* in the following transformation:



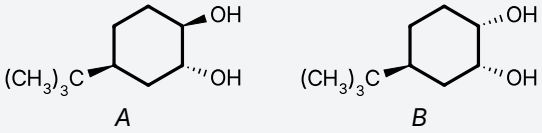
IFoS 2018 · Q7(a) Birch-type Na/NH_3 reduction of an octalone: major and minor products [10 marks]

Write the structure of the major and minor products formed in the following reaction and give a suitable explanation:



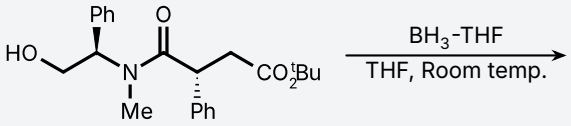
IFoS 2018 · Q7(c) Which 4-t-butylcyclohexane-1,2-diol resists periodate? [10 marks]

Of the following two compounds *A* and *B*, one cannot be oxidized by periodic acid. Identify it and justify your answer:



IFoS 2018 · Q8(b) BH_3 on an amide ester; OsO_4 on cyclopentene; ESR of a radical [15 marks]

(i) Write the structure of the product in the following reaction:



How many moles of BH_3 are needed to react with 2 moles of the starting material? 5

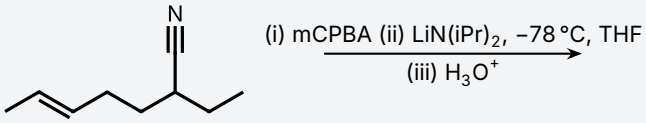
(ii) What stereoisomer would be formed from the reaction of cyclopentene with OsO_4 followed by hydrolysis? Explain. 5

(iii) Draw the ESR spectrum of $CH_3\dot{C}HOCH_2CH_3$. 5

2017

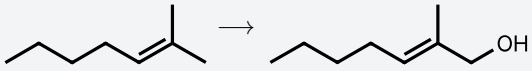
CSE 2017 · Q4(a) Epoxidation, then intramolecular opening by a nitrile anion [10 marks]

Predict the final product obtained after the following sequence of reactions and also suggest the corresponding plausible mechanistic pathway.

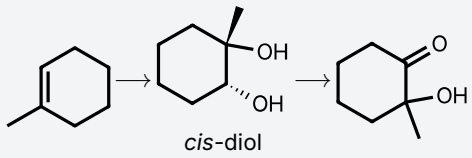


CSE 2017 · Q4(c) SeO_2 allylic oxidation; dihydroxylation and selective oxidation [10 marks]

Write the reagent(s) for the following conversions and write the mechanism for reaction (i).

(i) 

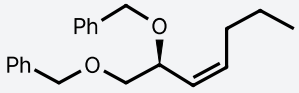
[6]

(ii) 

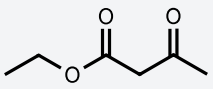
cis-diol [4]

CSE 2017 · Q7(b) Kishi dihydroxylation; ketal protection; Na/NH_3 on a terpene alcohol [15 marks]

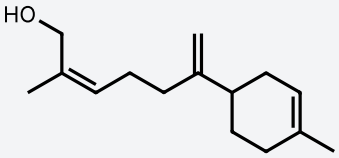
Identify the major product (*Z*) formed in the following reactions.

(i) 

OsO_4, pyridine, THF → (*Z*)

(ii) 

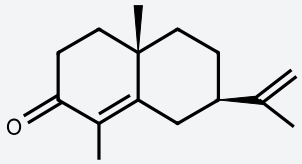
$LiAlH_4$, $C_2H_5-O-C_2H_5$ → (*Z*)
(1) $HO(CH_2)_3OH$, H^+ (2) $LiAlH_4$, (3) H_3O^+ → (*Z*)

(iii) 

Na, NH_3, C_2H_5OH → (*Z*)

CSE 2017 · Q8(c) Birch-type reduction of α-cyperone: trans ring fusion [10 marks]

Identify the product in the following reaction and provide the mechanism for the formation of the product.



(i) Na, NH_3, ether → (ii) NH_4Cl

IFoS 2017 · Q1(g) OsO_4 dihydroxylation: osmate ester and diol [5 marks]

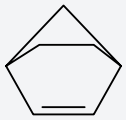
$$\rangle C{=}C\langle + OsO_4 \longrightarrow A \xrightarrow[\text{solution}]{\text{Aqueous ethanolic } NaHSO_3} B + (HO)_2OsO_2$$

Identify A and B.

2016

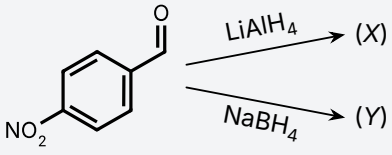
CSE 2016 · Q1(b) Norbornene and OsO_4: exo-cis diol [10 marks]

Identify the major product (*X*) and discuss its stereochemistry:


OsO_4, $NaHSO_3$ → (*X*)

CSE 2016 · Q1(e) 4-Nitrobenzaldehyde: $LiAlH_4$ against $NaBH_4$ [10 marks]

Give the structures of (*X*) and (*Y*):



CSE 2016 · Q3(b) MCPBA epoxidation of cis- and trans-but-2-ene [10 marks]

Discuss the stereoselectivity of products in the reaction of MCPBA with *cis*- and *trans*-butene.

CSE 2016 · Q4(c) Periodic acid oxidation of glucose and fructose [10 marks]

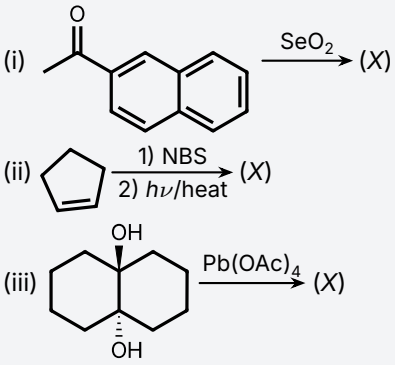
Glucose on periodic acid oxidation gives 5 molecules of formic acid, whereas fructose gives only 3 molecules of formic acid. Explain with reactions.

CSE 2016 · Q5(d) Na/liquid NH_3 reduction of oct-4-yne [10 marks]

Discuss the stereospecificity of reduction of $CH_3(CH_2)_2-C\equiv C-(CH_2)_2CH_3$ to alkene with sodium and liquid NH_3.

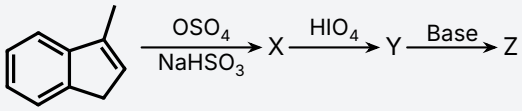
CSE 2016 · Q8(d) SeO_2, NBS and $Pb(OAc)_4$ reactions [15 marks]

Identify the major product (*X*) formed in the following reactions:



IFoS 2016 · Q5(c) 3-Methylindene: OsO_4, HIO_4, then base [5 marks]

Write the structure of X, Y and Z.



IFoS 2016 · Q8(b)(i) Periodic acid cleavage of an aldohexose [5 marks]

Explain how many molecules of formaldehyde and formic acid are formed in the reaction.

