II.4 Substitution Reactions

Civil Services 2016–2026: **32** parts, **300** marks · IFoS 2016–2025: **40** parts, **261** marks

Syllabus. SN1, SN2 and SNi mechanisms; neighbouring group participation; electrophilic and nucleophilic reactions of aromatic compounds including heterocyclic compounds: pyrrole, furan, thiophene and indole.

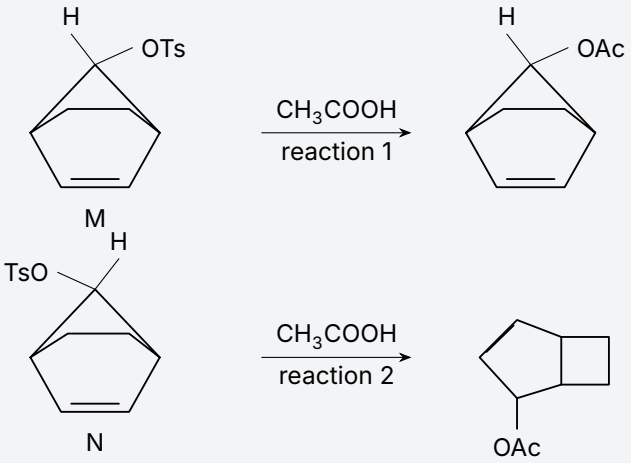
Marks	2016	2017	2018	2019	2020	2021	2022	2023	2024	2025	2026
CSE	45	30	35	15	10	20	35	35	40	10	25
IFoS	15	30	40	25	21	45	15	20	10	40	

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

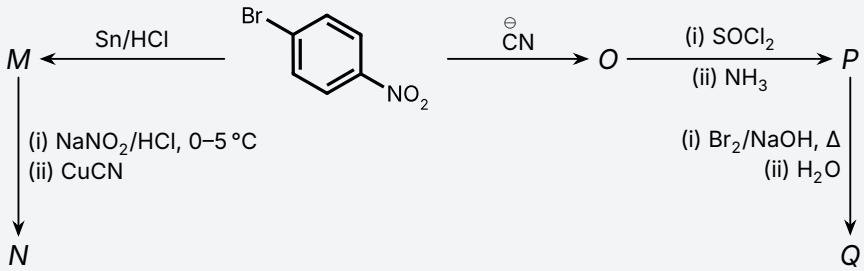
CSE 2026 · Q1(b) Solvolysis of anti- and syn-7-norbornenyl tosylates [10 marks]

Through a proper mechanism, explain the difference in the reactivity of M and N in the following solvolysis reactions.



CSE 2026 · Q2(a) p-Bromonitrobenzene: Sandmeyer and von Richter routes [15 marks]

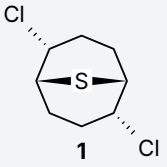
Write the structures of the major products M, N, O, P and Q formed in the following reaction sequence:



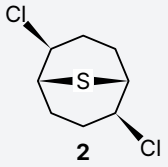
2025

CSE 2025 · Q4(c)(i) Two dichlorides with NaN_3: neighbouring sulfur [10 marks]

(i) Compounds 1 and 2 on reaction with NaN_3 yield same product but compound 1 reacts at room temperature while compound 2 reacts at 200 °C. Identify the product formed and explain the reasons for different reactivities of compounds 1 and 2:



1



2

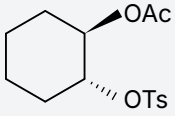
[10]

IFoS 2025 · Q1(c) Electrophilic substitution of heteroarenes [5 marks]

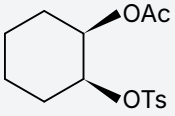
Giving appropriate explanation, compare the order of reactivity of pyrrole and thiophene towards an electrophile.

IFoS 2025 · Q2(a) Neighbouring acetate participation [10 marks]

Compare the rate of acetolysis of A and B giving suitable justification. Also give the product(s) of acetolysis in each case with mechanisms :



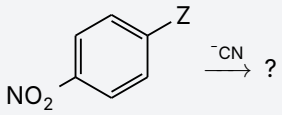
(A)



(B)

IFoS 2025 · Q4(b) Nucleophilic aromatic substitution [10 marks]

Complete the following reaction with mechanism :



IFoS 2025 · Q4(d) Pyrrole with chloroform and base [10 marks]

What is/are the products obtained in a reaction when pyrrole is reacted with chloroform in aqueous basic solution ? Write the mechanism of product(s) formation.

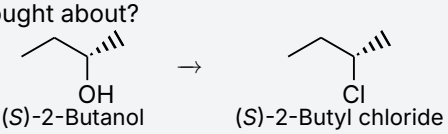
IFoS 2025 · Q8(c) Metalation of thiophene [5 marks]

Despite the lower electronegativity of sulphur, thiophene metallates as readily as furan. Why?

2024

CSE 2024 · Q1(c) (S)-2-Butanol to (S)-2-butyl chloride [10 marks]

How is the following conversion brought about?



(*S*)-2-Butanol → (*S*)-2-Butyl chloride

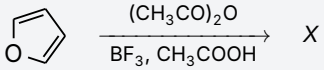
Explain its mechanism.

CSE 2024 · Q3(c)(ii) Indole at C-3; inertness of chlorobenzene [10 marks]

(ii) Account for the following:
(1) Indole undergoes electrophilic substitution to give 3-substituted product, but not 2-substituted product.
(2) Chlorobenzene does not undergo nucleophilic substitution reaction readily. 10

CSE 2024 · Q4(a) Furan with acetic anhydride and BF_3; Major products and mechanism type [15 marks]

(i) Consider the following reaction:



Name the product *X* and outline the mechanism indicating the rate-determining step. 10

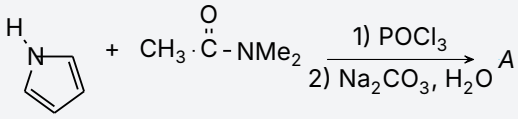
(ii) Indicate the major products of the following reactions and point out the mechanism as S_N1, S_N2, E1 or E2:
(1) $(CH_3)_3CBr + C_2H_5OH \xrightarrow[60\ ^\circ C]{Heat}$
(2) $CH_3CH{=}CHCl + NaNH_2 \longrightarrow$ 5

CSE 2024 · Q4(b)(ii) Energy profile: benzene to chlorobenzene [5 marks]

(ii) Draw the energy profile diagram for the conversion of benzene to chlorobenzene giving structures of transition states. 5

IFoS 2024 · Q3(a) Vilsmeier acylation of pyrrole [10 marks]

Complete the following reaction with detailed reaction mechanism :



2023

CSE 2023 · Q1(c) Methyl iodide with sodium azide: DMF against methanol [10 marks]

The reaction of methyl iodide with sodium azide is faster in N,N-dimethyl formamide (DMF) than in methanol. Explain.

CSE 2023 · Q2(b)(i) Hydrolysis of bis(2-chloroethyl) sulfide and of 1,5-dichloropentane [5 marks]

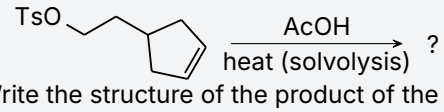
(i) (A) $ClCH_2CH_2SCH_2CH_2Cl \xrightarrow[k_1]{H_2O} HOCH_2CH_2SCH_2CH_2OH$ (B) $Cl(CH_2)_5Cl \xrightarrow[k_2]{H_2O} HO(CH_2)_5OH$
The rate of hydrolysis (k_1 and k_2) of the reaction (A) is much faster than that of (B). Explain. (5 marks)

CSE 2023 · Q2(b)(ii) Both glycosyl bromides give the β-glycoside [5 marks]

(ii) [(A) and (B) are the two anomeric 2,3,4,6-tetra-*O*-acetyl-D-glucopyranosyl bromides, Br equatorial in (A) and axial in (B); (C) is methyl 2,3,4,6-tetra-*O*-acetyl-*β*-D-glucopyranoside.]
The reaction of the compounds (A) and (B) with $AgClO_4$ in MeOH gives the same product (C). Explain. (5 marks)

CSE 2023 · Q2(c) Acetolysis of 2-(cyclopent-3-enyl)ethyl tosylate; Indole: electrophilic substitution at C-3, not C-2 [15 marks]

(i)



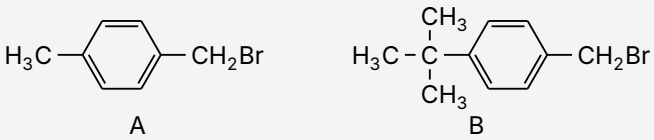
Write the structure of the product of the above reaction and provide suitable mechanism. (10 marks)

(ii) Write the preferred position (C-2 or C-3) in electrophilic substitution of indole. Explain your observation

with the help of resonance structures. (5 marks)

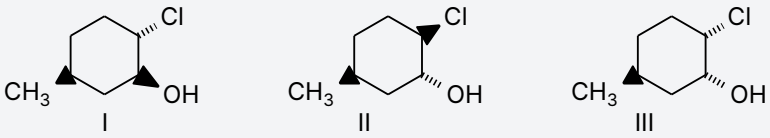
IFoS 2023 · Q1(d) Para-alkyl effects on benzyl solvolysis [5 marks]

Compare with proper explanation, the solvolysis behaviour of the following organic compounds :



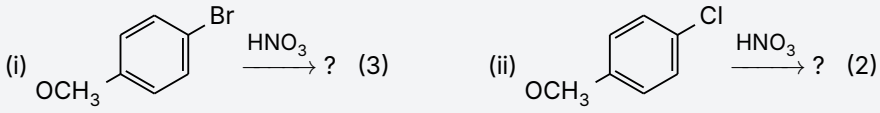
IFoS 2023 · Q2(b) Halohydrin cyclization and chair populations [10 marks]

Arrange the following molecules in the decreasing order of their epoxidation tendency with reason(s) :



IFoS 2023 · Q3(b) Nitration of p-bromoanisole; Nitration of p-chloroanisole [5 marks]

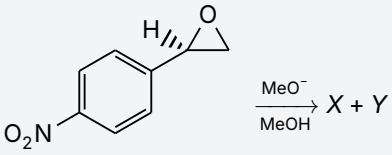
Complete the following reactions :



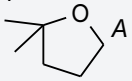
2022

CSE 2022 · Q1(b) (4-Nitrophenyl)oxirane with methoxide in methanol [10 marks]

Predict the structures of *X* and *Y*, and also mention the major product:



CSE 2022 · Q2(b)(i) 2,2-Dimethyltetrahydrofuran with one equivalent of HI [5 marks]

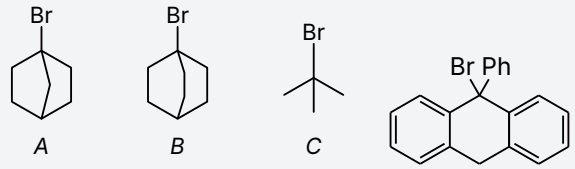
(i) What happens when the compound *A* is heated with one equivalent of HI? Give the structure of the product. Justify your answer:  *A* 5

CSE 2022 · Q3(b)(ii) p-Bromonitrobenzene to m-bromobenzoic acid [5 marks]

(ii) How will you convert *p*-bromonitrobenzene to *m*-bromobenzoic acid? Give the mechanism. 5

CSE 2022 · Q3(c)(ii) SN2 reactivity of four tertiary bromides [10 marks]

(ii) Arrange the following compounds in order of their increasing reactivity towards nucleophilic substitution through S_N2 mechanism. Assign the reason for the same also:



10

D

CSE 2022 · Q4(b)(ii) p-Nitrotoluene to m-nitrotoluene [5 marks]

(ii) How will you convert *p*-nitrotoluene to *m*-nitrotoluene? 5

IFoS 2022 · Q1(e) Substituent effects on aryl negative charge [5 marks]

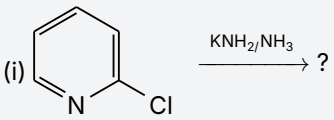
Why does $-NH_2$ at 'ortho' and 'para' position of the aromatic ring with respect to negatively charged groups cause their destabilization whereas $-NO_2$ at the same position has the stabilizing effect?

IFoS 2022 · Q1(f) Why DMSO accelerates many SN2 reactions [5 marks]

Polar aprotic solvents like DMSO favour the S_N2 reactions. Why?

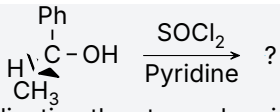
IFoS 2022 · Q3(a)(i) Amination of 2-chloropyridine [5 marks]

Complete the following reactions with their mechanisms:

(i) 

2021

CSE 2021 · Q2(c)(i) 1-Phenylethanol with $SOCl_2$ and pyridine [10 marks]

(i) 

Indicating the stereochemistry of the product, complete the above reaction with mechanism. 10

CSE 2021 · Q3(c)(ii) 3-Iodo-2,2-dimethylbutane with silver nitrate in hot ethanol [10 marks]

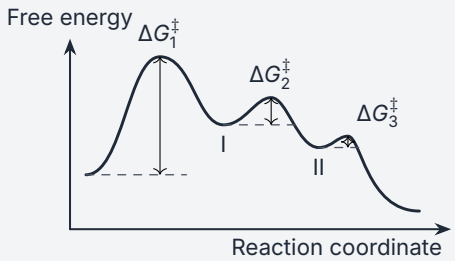
(ii) $CH_3-C(CH_3)_2-CHI-CH_3 \xrightarrow[EtOH,\ \Delta]{AgNO_3} ?$ 10

Complete the following reactions along with mechanisms.

IFoS 2021 · Q2(b) Hydrolysis of tert-butyl chloride [10 marks]

For the given reaction,

$$(CH_3)_3C{-}Cl + 2\,H_2O \longrightarrow (CH_3)_3C{-}OH + H_3O^+ + Cl^-$$



(i) Write the reaction mechanism for the above reaction.

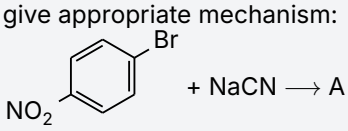
(ii) Give reasons for the formation of I and II as shown in the energy diagram.

IFoS 2021 · Q2(c)(i) p-Toluidine to m-bromotoluene [5 marks]

(i) How will you convert p-Toluidine into m-Bromotoluene by using appropriate reagents and conditions? 5

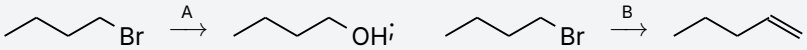
IFoS 2021 · Q3(d)(ii) Cyanide substitution on a nitroaryl halide [5 marks]

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



IFoS 2021 · Q4(c) Substitution versus elimination of a primary bromide; Alcohol to chloride with retention [10 marks]

(i) Write the reagents for following conversions and give suitable justification to support your answer. 5



(ii) Write a reaction for the conversion of 2° alcohol into 2° alkyl chloride with retention of configuration and formation of intimate ion pair. 5

IFoS 2021 · Q5(f) Nitration of indole [5 marks]

Can indole be nitrated using conc. HNO_3 and conc. H_2SO_4 mixture? If yes, then what are the products? If no, then how can indole be nitrated? Give the reaction with appropriate example.

IFoS 2021 · Q7(a)(i) A beta-chloroamine and sulfonyl chloride [5 marks]

(i) Suggest the reaction mechanism and product for the given reaction: 5

$$\text{Et–NH–CH}_2\text{–CH(Me)–Cl} \xrightarrow[H_2O]{NaOH} \; ? \; \xrightarrow[\text{Pyridine, }\Delta]{H_3C\text{–}C_6H_4\text{–}SO_2Cl} \; ?$$

IFoS 2021 · Q7(c)(i) Solvolysis of a tertiary allylic bromide [5 marks]

(i) Write the product and give the mechanism of the following reaction: 5

$$\text{1-bromo-1-ethylcyclohex-2-ene} \xrightarrow{EtOH} \text{Product(s)}$$

2020

CSE 2020 · Q1(a) Cycloheptatrienyl (tropylium) bromide: an ionic organic bromide [10 marks]

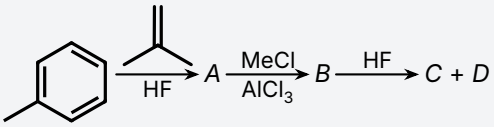
Generally alkyl halides are soluble in non-polar solvents and insoluble in water but cycloheptatrienyl bromide is insoluble in non-polar solvents but readily soluble in water. Explain this unusual behaviour of cycloheptatrienyl bromide.

IFoS 2020 · Q1(d) Why fluoride fails to displace iodide in acetone [5 marks]

Attempted displacement of iodide ion by fluoride in acetone usually fails. Why?

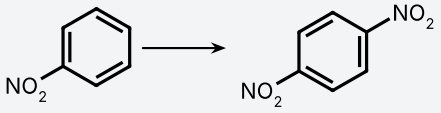
IFoS 2020 · Q4(c) Friedel–Crafts alkylation of toluene with isobutylene; HF isomerisation [10 marks]

Write the structure of the product (major) in each step and account for their formation in the following reactions:



IFoS 2020 · Q4(d) Nitrobenzene to p-dinitrobenzene [6 marks]

Carry out the following transformation:



2019

CSE 2019 · Q3(a) trans- and cis-2-Bromocyclopentanol with hydroxide [15 marks]

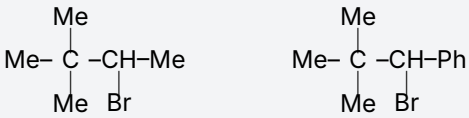
Formulate the following reactions and propose mechanism:

(i) *trans*-2-bromocyclopentanol $\xrightarrow{OH^-}$ Cyclopentene oxide

(ii) *cis*-2-bromocyclopentanol $\xrightarrow{OH^-}$ *trans*-1,2-cyclopentanediol

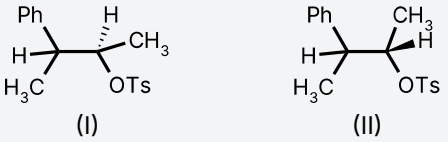
IFoS 2019 · Q1(b) Rearrangement in SN1 of a neopentyl-type bromide but not its phenyl analogue [5 marks]

Neopentyl-type bromide (I) undergoes rearrangement during S_N1 hydrolysis, but no such rearrangement takes place with its phenyl analogue (II). Explain:



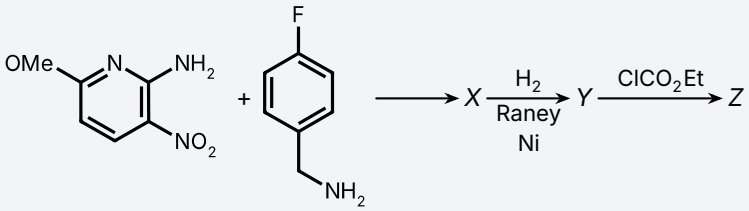
IFoS 2019 · Q2(b) Phenonium ion: acetolysis of 3-phenyl-2-butyl tosylates [10 marks]

2*S*,3*R*-3-Phenyl-2-butyl tosylate (I) yielded largely racemic 3-phenyl-2-butyl acetate on heating in acetic acid solution. In contrast, the 2*R*,3*R*-diastereomer (II) was converted to optically active 3-phenyl-2-butyl acetate. Explain:



IFoS 2019 · Q3(b) SNAr, nitro reduction and carbamate formation (X, Y, Z) [10 marks]

Complete the following conversion by identifying the compounds *X*, *Y* and *Z*. Briefly mention the type of reaction involved in each step:



2018

CSE 2018 · Q5(b) Allylic SN1: kinetic and thermodynamic acetates [10 marks]

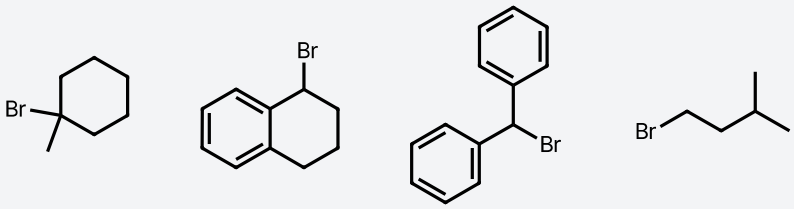
Two substitution products result from the reaction of 3-chloro-3-methyl-1-butene with sodium acetate ($CH_3COO-Na^+$) in acetic acid under S_N1 conditions. Identify the products. Indicate the thermodynamic product and kinetic product.

CSE 2018 · Q6(b) Acetolysis of threo- and erythro-3-phenyl-2-butyl tosylates [15 marks]

Write the product(s) with proper stereochemical outcome of acetolysis of each of *threo*- and *erythro*-3-phenyl-2-butyltosylate giving the reaction pathway in each case.

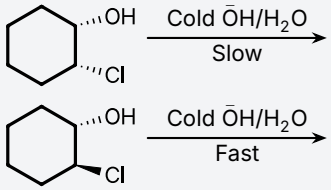
CSE 2018 · Q6(d) Order of SN1 solvolysis in aqueous formic acid [10 marks]

Arrange the following compounds in order of their decreasing reaction rate of substitution with aqueous formic acid and justify your answer :



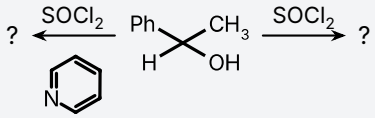
IFoS 2018 · Q1(e) Diastereomeric chlorohydrins with cold hydroxide: slow and fast [5 marks]

Account for the difference in reactivity of the following two reactions based on diastereomeric chlorohydrins. Write the product in each case:



IFoS 2018 · Q2(a) $SOCl_2$ on (R)-1-phenylethanol with and without pyridine: SNi versus SN2 [5 marks]

Predict the product(s) of the following reactions with proper stereochemical outcome and denote the corresponding pathways (abbreviated):



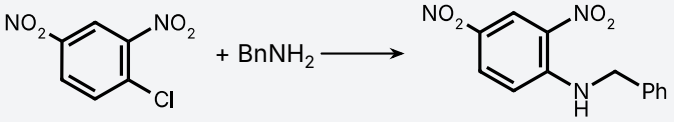
IFoS 2018 · Q2(d) Hydrolysis of S,S- and S,R-2-acetoxycyclohexyl tosylates: neighbouring group participation [10 marks]

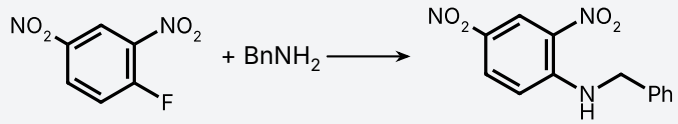
What type of mechanistic pathway is involved in each case of hydrolysis of *S*, *S*- and *S*, *R*-2-acetoxycyclohexyl tosylate, separately? Which one reacts at a faster rate and why? Write the structure of the product(s) with proper stereochemical outcome and mention *R*/*S* to the chiral carbons. Write the structure of the intermediate also (where applicable).

IFoS 2018 · Q2(f) SNAr energy profiles: chloro- versus fluoro-2,4-dinitrobenzene with $BnNH_2$ [5 marks]

Using the same coordinate system, draw two separate energy diagrams for the following two reactions. How can you denote (abbreviated form) such reactions?

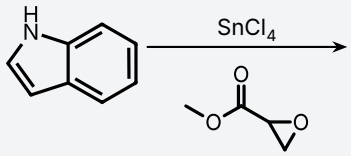
(i)



(ii) 

IFoS 2018 · Q3(e) Indole with methyl glycidate and $SnCl_4$ [5 marks]

Write the structure of the product of the following reaction and the corresponding mechanistic pathway:



IFoS 2018 · Q4(a) von Richter reaction of 4-bromonitrobenzene [5 marks]

When 4-bromonitrobenzene is reacted with cyanide ion, the product is devoid of any nitrogen. Write the structure of the product, name the reaction and write the corresponding mechanism.

IFoS 2018 · Q4(e) Bromination of salicylic acid in acetic acid [5 marks]

What happens when salicylic acid is reacted with bromine in acetic acid? Justify your answer.

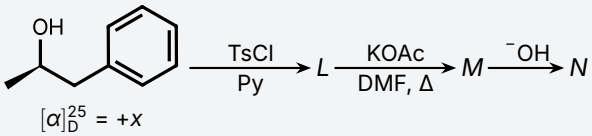
2017

CSE 2017 · Q3(b) Tertiary alcohol with two identical alkyl groups; Lucas test [10 marks]

Write a method of preparation of a tertiary alcohol containing two identical alkyl groups. Write one method for distinguishing primary, secondary and tertiary alcohols.

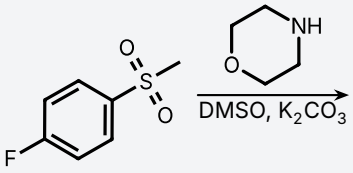
CSE 2017 · Q3(c) Tosylation, SN_2 by acetate and hydrolysis: a Walden cycle [10 marks]

Write the stereo structures of *L* to *N* and comment on the specific rotation of *N*. Specific rotation of the starting alcohol is $+x$.



CSE 2017 · Q3(e) Morpholine and 4-fluorophenyl methyl sulfone: SNAr [10 marks]

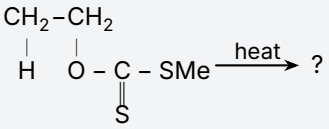
Write the structure of the product of the following reaction and depict the mechanism.



IFoS 2017 · Q2(a) Solvolysis of t-BuBr in aqueous methanol; Chugaev elimination [10 marks]

(i) The rate of hydrolysis of $(CH_3)_3CBr$ in 50% aqueous methanol is thousand times faster than that in pure methanol – explain. 5

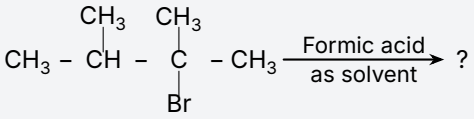
(ii) Mention the product(s) in the following reaction. Elucidate your answer.



5

IFoS 2017 · Q2(d) 2-Bromo-2,3-dimethylbutane in formic acid [10 marks]

Give the mechanistic steps and mark the major product of the following reaction:



IFoS 2017 · Q8(b) Friedel–Crafts routes to 4-oxo-4-phenylbutanoic acid and isobutylbenzene [10 marks]

Starting from benzene, how will you prepare the following employing Friedel-Crafts reaction?

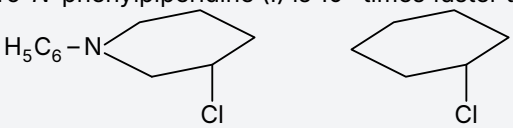
(i) 4-oxo-4-phenylbutanoic acid.

(ii) Isobutyl benzene.

2016

CSE 2016 · Q1(c) Neighbouring nitrogen: aziridinium ion [10 marks]

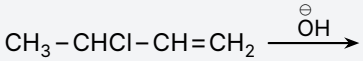
Explain why hydrolysis of 3-chloro-*N*-phenylpiperidine (I) is 10^4 times faster than cyclohexylchloride (II):



(I) (II)

CSE 2016 · Q1(d) 3-Chlorobut-1-ene and hydroxide: allylic substitution [10 marks]

For the reaction given below, write the structures of major and minor products, and discuss the mechanism of their formation:

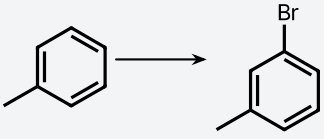


CSE 2016 · Q2(a) Sulfonation of naphthalene: kinetic and thermodynamic control [15 marks]

In the sulfonation of naphthalene, discuss the formation of kinetically and thermodynamically controlled products under different conditions with energy level diagram.

CSE 2016 · Q3(a) Toluene to m-bromotoluene: an amino group as a temporary director [10 marks]

How will you carry out the following conversion?

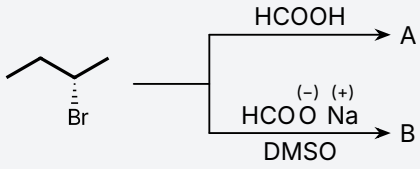


IFoS 2016 · Q1(c) Quinuclidine against triethylamine with ethyl iodide [5 marks]

Quinuclidine reacts much faster with ethyl iodide than triethyl amine in S_N2 reaction. Explain.

IFoS 2016 · Q2(a)(i) (S)-2-Bromobutane with HCOOH and with $HCOO^-Na^+$/DMSO [5 marks]

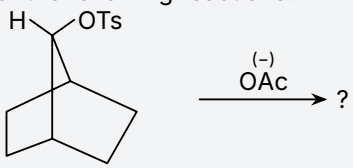
Write the outcome of the reaction and predict the reaction to S_N1 or S_N2 in each case.



IFoS 2016 · Q2(a)(ii) 7-Norbornyl and anti-7-norbornenyl tosylates: participation of a C=C [5 marks]

Show the products of the following reactions:

(I)



(II)

