II.7 Named Reactions and Rearrangements

Civil Services 2016–2026: **65** parts, **820** marks · IFoS 2016–2025: **81** parts, **624** marks

Syllabus. (a) Pinacol-pinacolone, Hofmann, Beckmann, Baeyer-Villiger, Favorskii, Fries, Claisen, Cope, Stevens and Wagner- Meerwein rearrangements. (b) Aldol condensation, Claisen condensation, Dieckmann, Perkin, Knoevenagel, Wittig, Clemmensen, Wolff-Kishner, Cannizzaro and von Richter reactions; Stobbe, benzoin and acyloin condensations; Fischer indole synthesis, Skraup synthesis, Bischler-Napieralski, Sandmeyer, Reimer-Tiemann and Reformatsky reactions.

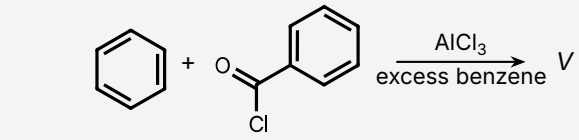
Marks	2016	2017	2018	2019	2020	2021	2022	2023	2024	2025	2026
CSE	95	100	50	140	65	45	75	40	70	45	95
IFoS	60	45	40	90	64	50	75	70	60	70	

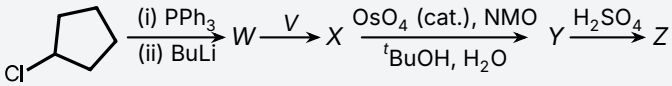
How to use this chapter. Read every question once and mark the ones that repeat. Pick three, write them by hand against the clock (about 7 minutes for 10 marks), then compare with the model answers on vkcscience.com.

2026

CSE 2026 · Q1(c) Friedel–Crafts, Wittig, dihydroxylation and pinacol rearrangement [10 marks]

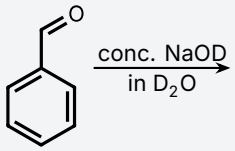
Identify the major products V, W, X, Y and Z in the following reaction sequences:



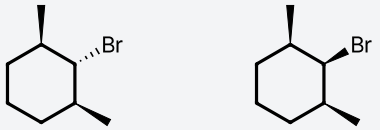


CSE 2026 · Q2(b) Cannizzaro in D_2O; E2 in rings; 1,2- vs 1,4-addition [15 marks]

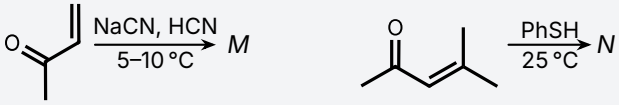
(i) Write the products formed in the following reaction along with the mechanism of their formation.



(ii) Which one of the following two compounds, Y and Z, can undergo elimination reaction under E2 conditions? Explain.



(iii) Write the major products M and N formed in the following reactions:

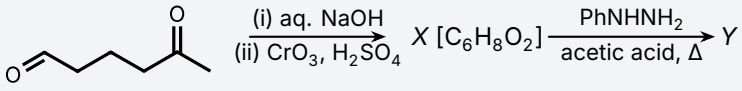


CSE 2026 · Q3(a) Tollens condensation; aldol, Jones oxidation and Fischer indole [15 marks]

(i) Write the structure of the major products of the following reaction and write the mechanism of their formation:

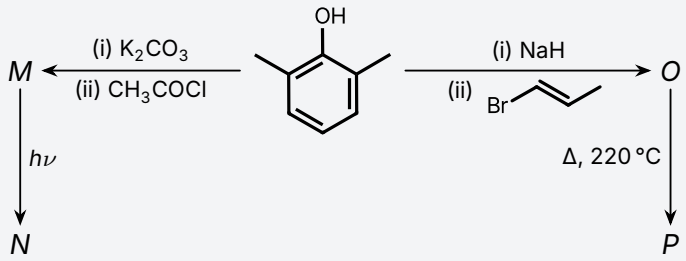
$$CH_3CHO \ + \ HCHO \text{ (excess)} \xrightarrow{\text{aq. NaOH}}$$

(ii) Write the structures of the major products X and Y formed in the following reaction sequence. Provide a mechanism for the conversion of X to Y.



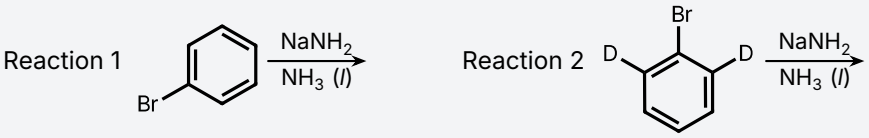
CSE 2026 · Q3(b) 2,6-Dimethylphenol: photo-Fries and para-Claisen rearrangement [15 marks]

Write the structures of the major products M, N, O and P in the following reaction sequence. Suggest a mechanism for the conversion of O to P.

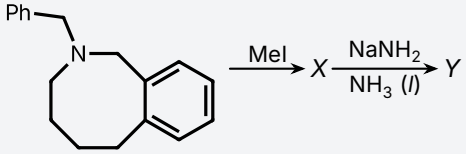


CSE 2026 · Q3(c) Benzyne isotope effect; Stevens ring enlargement [20 marks]

(i) Write the structures of the products formed in the following reactions. Which one of these two reactions would proceed faster? Justify your answer.

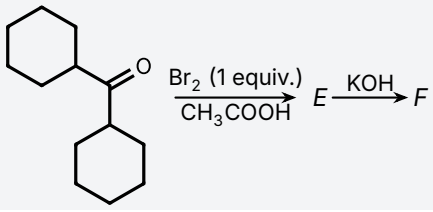


(ii) Write the structures of the major products X and Y formed in the following reaction sequence. Write a suitable mechanism for the formation of Y from X.



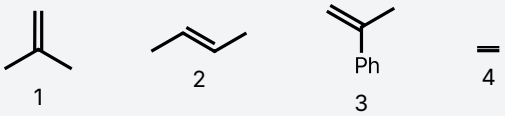
CSE 2026 · Q4(c) Favorskii rearrangement; bromine addition in methanol; indole anions [20 marks]

(i) Write the structures of the major products E and F of the following reaction sequence. Write the mechanism of formation of F from E.

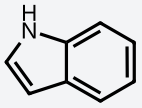


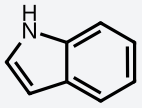
(ii) Consider the reaction given below: $R^1R^2C{=}CR^3R^4 \xrightarrow[MeOH]{Br_2} R^1R^2C(OMe){-}CR^3R^4Br$

Write the order of increasing reactivity of the following alkenes towards the above reaction.



(iii) Write the major products formed in the following reactions:

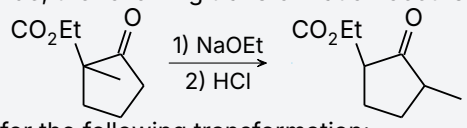
Reaction 1  (i) ^{n}BuLi (ii) CO_2 (iii) H^+

Reaction 2  (i) ^{n}BuMgBr (ii) CO_2 (iii) H^+

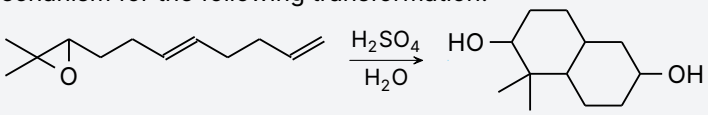
2025

CSE 2025 · Q2(a) Ester shift with sodium ethoxide; cyclisation of an epoxy-diene [15 marks]

(i) In the presence of sodium ethoxide, the following transformation occurs. Explain:

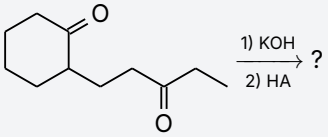


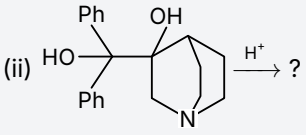
(ii) Propose a suitable mechanism for the following transformation:

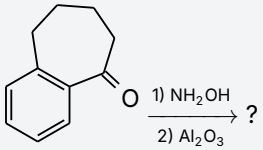


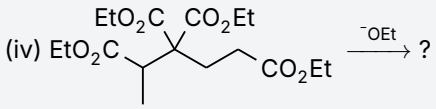
CSE 2025 · Q2(c) Products of four reactions [20 marks]

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

(i) 

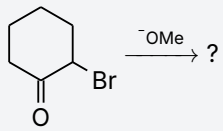
(ii) 

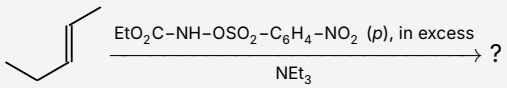
(iii) 

(iv) 

CSE 2025 · Q3(a)(i) Products of two reactions [10 marks]

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

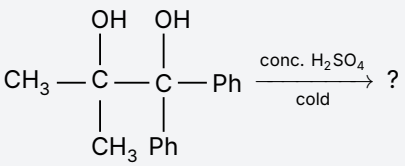
(1) 

(2) 

[10]

IFoS 2025 · Q1(f) Medium-dependent pinacol rearrangement [5 marks]

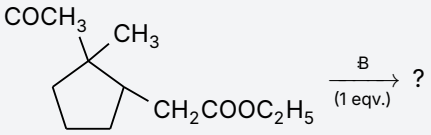
Write the products in the following transformations :



and, with CH_3COOH/conc. $H_2SO_4 \longrightarrow$?

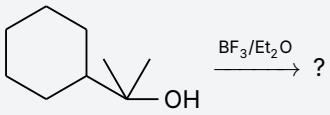
IFoS 2025 · Q1(h) Intramolecular Claisen condensation [5 marks]

Giving the most plausible mechanism, complete the following reaction :



IFoS 2025 · Q2(b) Dehydration with carbocation rearrangement [10 marks]

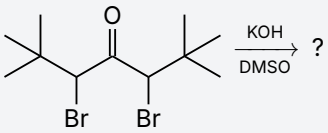
Complete the following reaction along with the mechanism. Also indicate the product spread with suitable reasons :



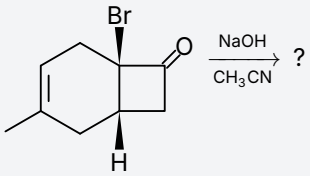
IFoS 2025 · Q2(c) Favorskii reactions of two alpha-haloketones [10 marks]

Giving the products, complete the following reactions along with their mechanisms :

(i)



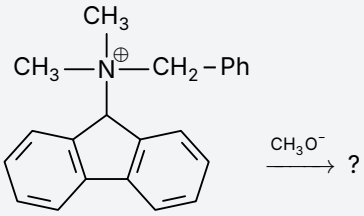
(ii)



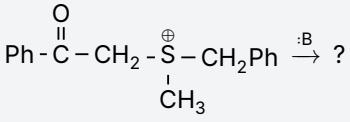
IFoS 2025 · Q3(a) Stevens rearrangements of two ylides [10 marks]

Write the products with mechanisms in the following reaction sequences :

(i)



(ii)

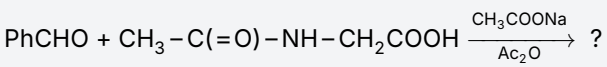


IFoS 2025 · Q3(b) Knoevenagel condensation [10 marks]

Write the reaction of diethyl malonate with acetaldehyde in the presence of piperidine (as catalyst). Also write the mechanism for the product(s) formation.

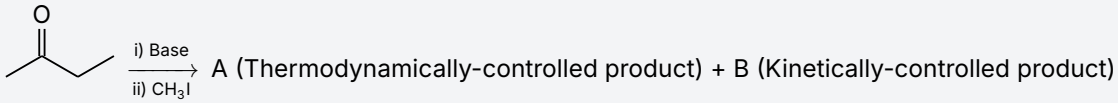
IFoS 2025 · Q3(c) Erlenmeyer–Plöchl azlactone synthesis [10 marks]

Giving mechanism, complete the following reaction :



IFoS 2025 · Q3(d) Regioselective ketone alkylation [10 marks]

In the following reaction :



(i) Identify A and B.

(ii) Write a name of a base in each case to form A and B regioselectively.

(iii) Write the nature of solvent and the reaction temperature required for regioselective formation of A and B.

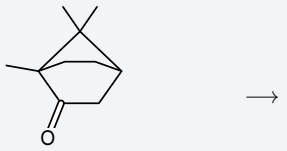
(iv) Give the mechanism of formation of A and B.

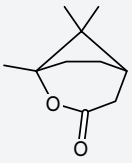
2024

CSE 2024 · Q1(d) Name and reagent for five conversions [10 marks]

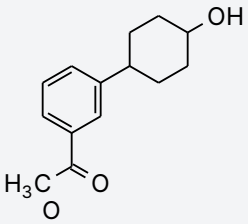
Write the name of the reaction and reagent required for the following conversions:

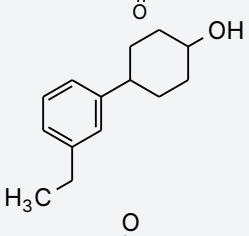
(i)



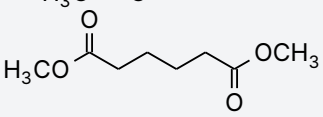


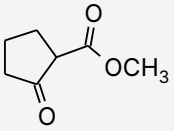
(ii)





(iii)





(iv) $CH_3-CH_2-\overset{+}{N}Me_3 \longrightarrow H_2C=CH_2 + NMe_3$

(v) $C_6H_5-CHO \longrightarrow C_6H_5-COO^- + C_6H_5-CH_2OH$

CSE 2024 · Q2(b)(i) Benzaldehyde with diethyl malonate and pyridine [10 marks]

(i) Identify the major product *X* in the following reaction:

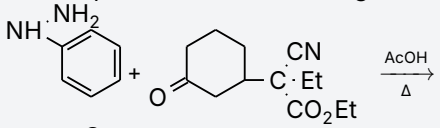
$$C_6H_5-CHO + CH_2(COOC_2H_5)_2 \xrightarrow{\text{Pyridine}} X$$

Explain its mechanism. Name the reaction. 10

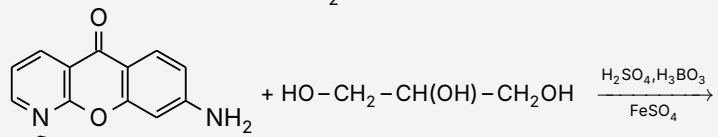
CSE 2024 · Q2(c) Products of three reactions; 2-Methylpent-2-enoic acid by the Reformatsky reaction [20 marks]

(i) Write the product of the following reactions:

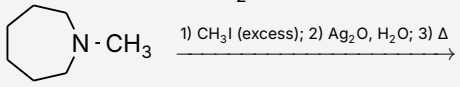
(A)



(B)



(C)



15

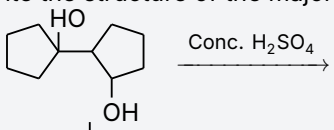
(ii) How is the following compound prepared using a Reformatsky reaction?

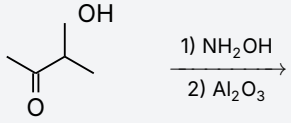
$$CH_3CH_2CH{=}C(CH_3){-}COOH$$

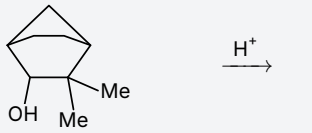
5

CSE 2024 · Q4(c) Major products of three rearrangements; Chlorodifluoromethyl phenyl ketone with Ac_2O / AcONa [20 marks]

(i) Write the structure of the major product(s) formed in the following reactions:

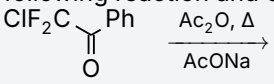
(A) 

(B) 

(C) 

10

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



10

CSE 2024 · Q8(b)(i) Ring opening of 2,2-dimethylcyclopropanone by methoxide [10 marks]

(i) 2,2-Dimethyl cyclopropanone undergoes ring opening when attacked by methoxide ion and the product obtained possesses the following spectral data:

IR (ν, cm^{-1}): 1740, 1160

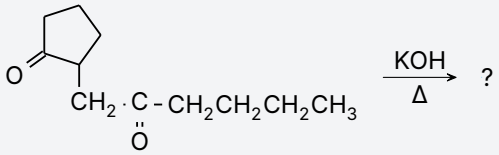
^1H NMR (δ): 3.6 (3H, s), 1.2 (9H, s)

Mass (m/z): 116, 85, 59, 31

Deduce the structure of the product with reasons. Write down the structure of another possible product. [10]

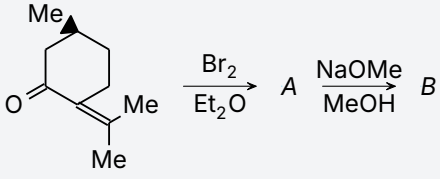
IFoS 2024 · Q1(e) Intramolecular aldol condensation [5 marks]

Giving mechanism, write down the product(s) in the following chemical transformation :



IFoS 2024 · Q1(f) Pulegone to a ring-contracted ester [5 marks]

Identify *A* and *B* in the following reaction/rearrangement with mechanism :



IFoS 2024 · Q1(h) Hydrazine reductions [5 marks]

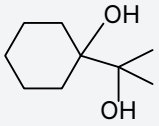
Give the products in the following reaction sequences :

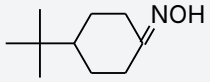
(i) $CH_3-CHBr-CH_2-COCH_3 \xrightarrow[DMSO,\ Heat]{NH_2NH_2/t\text{-}BuO^- K^+} ?$

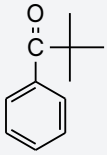
(ii) $R-CO-CO-R \xrightarrow[Alc.\ KOH,\ Glycol]{NH_2-NH_2} ?$

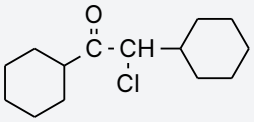
IFoS 2024 · Q3(b) Five rearrangement products [15 marks]

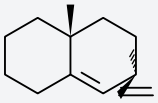
Write the major product(s) of each of the following rearrangements with justification :

(i)  $\xrightarrow{Aq.\ HClO_4}$?

(ii)  $\xrightarrow{SO_2Cl_2}$?

(iii)  $\xrightarrow{CF_3CO_3H}$?

(iv)  $\xrightarrow[2)\ H_3O^+]{1)\ NaOH}$?

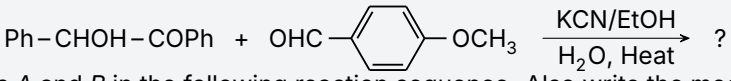
(v)  $\xrightarrow{H_2SO_4}$?

IFoS 2024 · Q4(b) Stobbe condensation [10 marks]

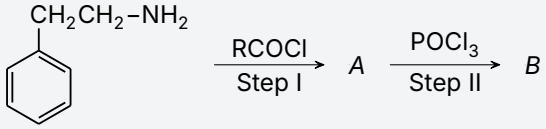
Write the product of the reaction between cyclohexanone and diethyl succinate in the presence of a strong base followed by treatment with aqueous acid. Also give the mechanism of this transformation.

IFoS 2024 · Q4(c) Benzoin exchange in cyanide; Bischler–Napieralski cyclization [20 marks]

(i) Write the product(s) in the following reaction sequence along with the mechanism : 10

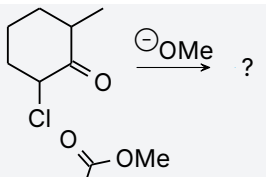


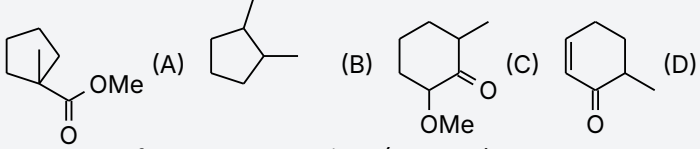
(ii) Identify the products *A* and *B* in the following reaction sequence. Also write the mechanism of Step II : 10



2023

CSE 2023 · Q1(e) 2-Chloro-6-methylcyclohexanone with methoxide; Name reaction that gives nitrogen as a by-product [10 marks]

(i)  $\xrightarrow{\ominus OMe}$?



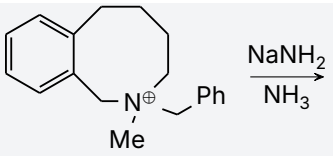
Identify the major product of the above reaction. (5 marks)

(ii) Identify the name reaction which produces nitrogen as a byproduct.

(A) Fischer Indole synthesis (B) von Richter reaction (C) Stobbe reaction (D) Bischler-Napieralski reaction

(5 marks)

CSE 2023 · Q4(b) Cyclic benzylammonium salt with $NaNH_2$ / NH_3 [10 marks]



Complete the above reaction and give suitable mechanism.

CSE 2023 · Q4(c) Crossed aldol: butanone and acetaldehyde; Benzonitrile from benzene [20 marks]

(i) $CH_3COCH_2CH_3 + CH_3CHO \xrightarrow{\ominus OH}$?
How many *β*-hydroxy carbonyl compounds may be theoretically formed in the above reaction? Write the structure of the products formed. (10 marks)

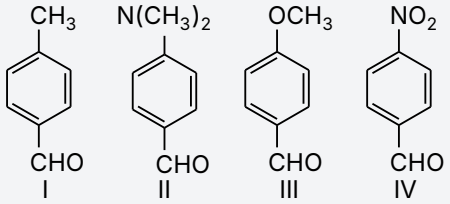
(ii) Write the synthesis of benzonitrile starting from benzene (Hint: may involve more than one step). (10 marks)

IFoS 2023 · Q1(f) Why nucleophilic shifts are common [5 marks]

Explain why nucleophilic 1,2 shifts are more common than 1,2 electrophilic or free radical shifts.

IFoS 2023 · Q1(h) Substituent effects in Cannizzaro reaction [5 marks]

Arrange the following aldehydes towards their ease of reactivity in Cannizzaro's reaction in the decreasing order :

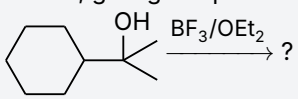


IFoS 2023 · Q2(a) Third- and fourth-order Cannizzaro kinetics [10 marks]

Cannizzaro's reaction exhibits third order kinetic at low base concentration and fourth order kinetic at higher base concentration. Explain the mechanism of Cannizzaro in the light of above kinetic data.

IFoS 2023 · Q2(c) Lewis-acid dehydration and rearrangement [10 marks]

Complete the following reaction with mechanism, giving the plausible reasons for product spread :



IFoS 2023 · Q2(d) Butanone phenylhydrazone and Fischer cyclization [10 marks]

Give the product(s) of the condensation reaction of 2-butanone with phenylhydrazine along with the mechanism.

IFoS 2023 · Q3(e) Self-condensation of diethyl succinate [10 marks]

Complete the following reaction with mechanism :

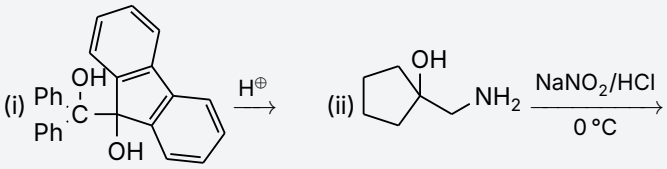
$$EtO_2C-CH_2-CH_2-CO_2Et\ (2\ eq.)\ +\ \overset{\ominus}{}OEt \rightarrow\ ?$$

IFoS 2023 · Q4(d) Knoevenagel condensation [5 marks]

Butanal reacts with ethyl cyanoacetate in the presence of base. Give the product(s) of this reaction along with mechanism.

IFoS 2023 · Q4(e) Pinacol and Tiffeneau–Demjanov rearrangements [5 marks]

Write the product(s) of the following reactions :



IFoS 2023 · Q4(g) Two substrates, one Favorskii intermediate [10 marks]

Write the product(s) of reaction of 1-chloro-3-phenyl-2-propanone and 1-chloro-1-phenyl-2-propanone CH_3ONa/CH_3OH separately. Explain the mechanism involved.

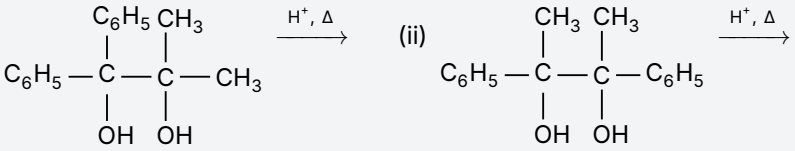
2022

CSE 2022 · Q1(c) The reaction that is not a condensation, and its mechanism [10 marks]

Out of the following list of reactants along with the reagents, identify the reaction which is not a condensation reaction. Propose a suitable mechanism for the products formed in this reaction:
(i) Acetaldehyde is reacted with dilute KOH
(ii) Benzaldehyde is reacted with acetic anhydride in presence of sodium acetate
(iii) Benzaldehyde is reacted with malonic ester in presence of a base
(iv) Benzaldehyde is reacted with concentrated KOH

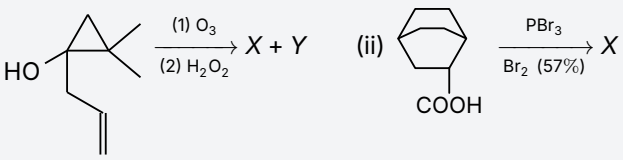
CSE 2022 · Q1(d) Acid-catalysed rearrangement of two phenyl-substituted 1,2-diols [10 marks]

Write down the structure(s) of the product(s) obtained in the following reactions. Provide suitable justification and propose the mechanisms:



CSE 2022 · Q2(a) Products X and Y in three reactions [15 marks]

Predict the products *X* and *Y* in the following reactions:



(iii) $CH_3-CH(CH_3)-CH_3 \xrightarrow[127\,^\circ C]{Br_2/h\nu} X + Y$

5 × 3 = 15

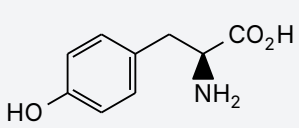
CSE 2022 · Q2(c) Matching three heterocycle syntheses; mechanism of the indole synthesis; L-Dopa from L-tyrosine [20 marks]

(i) Match the following for the synthesis of class of compounds listed in Set-I with the reactants and reagents of Set-II:

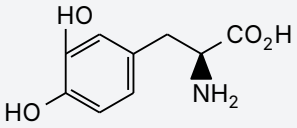
(A)	Quinoline	(1)	Cinnamaldehyde, hydroxylamine, P_2O_5
(B)	Isoquinoline	(2)	Acetaldehyde, phenylhydrazine, acid
(C)	Indole	(3)	Glycerol, aniline, acid, nitrobenzene
		(4)	α-Halocarbonyl compound, thiourea

Propose the mechanism for the synthesis of indole. 10

(ii) Write the reaction sequence for the synthesis of L-dopa (*B*), a drug for the treatment of Parkinson's disease, from L-tyrosine (*A*), an α-amino acid: 10



A



B

CSE 2022 · Q4(c) Phenol to coumarin [20 marks]

By using appropriate reagents and conditions, how will you convert phenol into coumarin? Give suitable mechanism for this transformation.

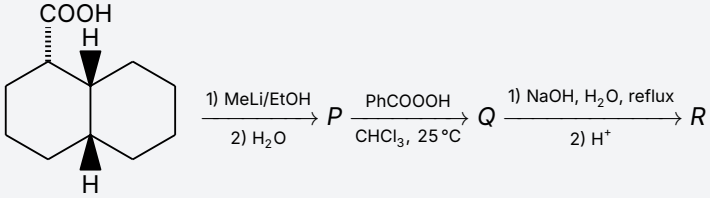
IFoS 2022 · Q1(g) Rearrangement during silver-assisted solvolysis [5 marks]

Write the major product obtained in the following reaction. Also substantiate your answer with mechanism:

2-Iodo-3,3-dimethylbutane $\xrightarrow[\text{EtOH, heat}]{AgNO_3}$?

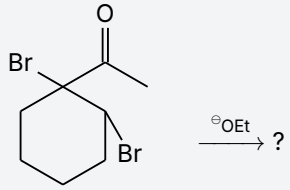
IFoS 2022 · Q1(h) Organolithium and Baeyer–Villiger sequence [5 marks]

Identify the products *P*, *Q* and *R* in the following chemical sequence:



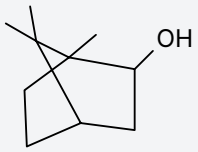
IFoS 2022 · Q2(b) Favorskii rearrangement of a dibromoketone [10 marks]

Complete the following reaction. Also write its possible mechanism along with the name of the reaction involved:



IFoS 2022 · Q2(c) Rearrangement of a bornane alcohol [10 marks]

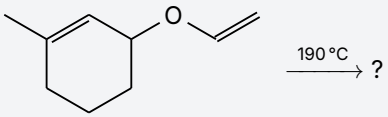
Write the product(s) of the reaction of alcohol (*A*) with acid (H^+) along with the mechanism. Also give the name of the reaction:



A

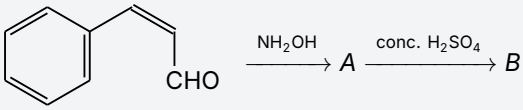
IFoS 2022 · Q2(d) Claisen rearrangement of an allyl vinyl ether [5 marks]

While naming the process involved, complete the following reaction along with its push and pull arrows mechanism:



IFoS 2022 · Q3(c) Cinnamaldoxime rearrangement and ring closure [10 marks]

Write the products *A* and *B* in the following sequence of reactions. Give the mechanism of second reaction only and also write the name of this reaction:



IFoS 2022 · Q4(a) Claisen condensation followed by cyclization [10 marks]

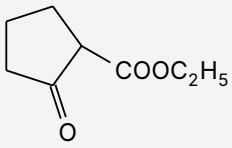
Complete the given reaction and provide mechanism for each step:

$$C_6H_5{-}C(CH_3)(OH){-}CO{-}CH_3 \;+\; (COOC_2H_5)_2 \xrightarrow[2)\ HOH/HCl]{1)\ C_2H_5ONa/C_2H_5OH} A \xrightarrow{HOH/H^+} B$$

IFoS 2022 · Q4(b) Dieckmann cyclization of diethyl adipate [10 marks]

Provide the name and mechanism for the given reaction:

$$C_2H_5O{-}CO{-}(CH_2)_3{-}CH_2{-}CO{-}OC_2H_5 \xrightarrow[2)\ H_2O/HCl]{1)\ C_2H_5ONa/C_2H_5OH}$$



IFoS 2022 · Q4(c) Cobalt-catalysed hydroformylation [10 marks]

Propose the mechanism for the following reaction:

$$2\,CH_3CH{=}CH_2 + 2\,CO + H_2 \xrightarrow{Co_2(CO)_8} CH_3CH_2CHO + CH_3CH(CHO)CH_3$$

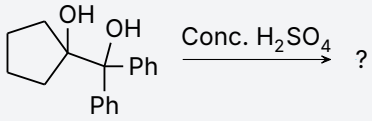
2021

CSE 2021 · Q1(b) Benzyltrimethylammonium salt with sodium amide at low and at high temperature [10 marks]

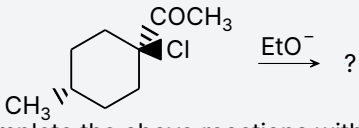
$$(CH_3)_3\overset{+}{N}{-}CH_2{-}C_6H_5 \qquad X^-$$

Discuss the product(s) formation when above quaternary ammonium salt is treated with sodium amide at low temperature and at high temperature.

CSE 2021 · Q3(a) 1-(Hydroxydiphenylmethyl)cyclopentanol with conc. H_2SO_4; 1-Acetyl-1-chloro-4-methylcyclohexane with ethoxide [20 marks]

(i) 

10

(ii) 

10

Complete the above reactions with mechanisms.

CSE 2021 · Q4(c) A Wittig reaction and a Fischer indole synthesis; Pairs that give an α,β-unsaturated carbonyl compound with base [15 marks]

(i) I. $PhCH_2Cl \xrightarrow{(1)\ (C_6H_5)_3P;\ (2)\ RLi;\ (3)\ \text{cyclohexanone}} ?$ II. $PhNHNH_2$ + cyclohexanone $\xrightarrow{\text{Glacial acetic acid}} ?$

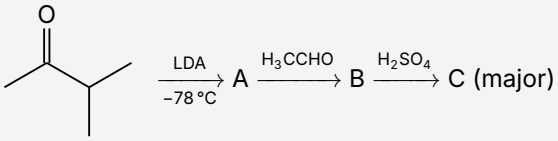
Predict the product in the above chemical conversions and also identify the name reaction involved. 10

(ii) Which of the following pair(s) gives α,β-unsaturated carbonyl compound in presence of base? Justify the answer.

I. HCHO and PhCHO II. PhCHO and $Ph-CH(CH_3)-CHO$ III. PhCHO and CH_3CH_2CHO IV. HCHO and PhCOPh 5

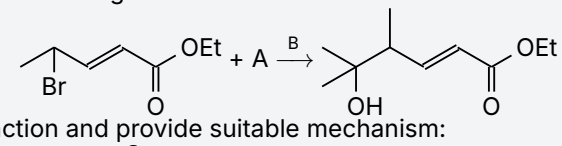
IFoS 2021 · Q1(d) Kinetic enolate aldol sequence [5 marks]

Complete the following reaction sequence and give suitable mechanisms for the formation of the major products:

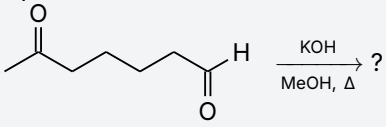


IFoS 2021 · Q3(b) Carbon–carbon bond formation from a bromoester; Intramolecular aldol condensation [10 marks]

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



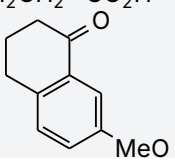
(ii) Complete the following reaction and provide suitable mechanism: 5



IFoS 2021 · Q3(d)(i) Haworth synthesis of a methoxytetralone [5 marks]

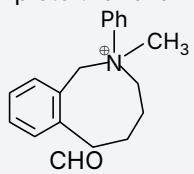
(i) Complete the following reactions sequence: 5

Anisole + A $\xrightarrow{SnCl_4}$ 4-$MeOC_6H_4-CO-CH_2CH_2-CO_2H$ $\xrightarrow{B}$ 4-$MeOC_6H_4-CH_2CH_2CH_2-CO_2H$ $\xrightarrow{C}$

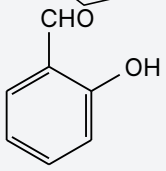


IFoS 2021 · Q4(e) Three rearrangement and condensation sequences [5 marks]

Complete the following reactions:

(i) 

$\xrightarrow[NH_3]{NH_2^{\ominus}}$?

(ii) 

$+ CH_3-CO-CH_2-CO-OEt \xrightarrow{\text{Piperidine}}$? $\xrightarrow[\text{(2) Piperidine } Br_2]{\text{(1) PhCHO}}$?

(iii) $Ph_2C(OH)-C(OH)(CH_3)_2 \xrightarrow[+ \text{ a trace of } H_2SO_4]{AcOH}$?; $Ph_2C(OH)-C(OH)(CH_3)_2 \xrightarrow{\text{cold } H_2SO_4}$?

IFoS 2021 · Q5(a) Condensation of diethyl succinate [5 marks]

Complete the following reactions sequence and give the mechanism of the STEP 1.

$$EtO_2C-CH_2-CH_2-CO_2Et \xrightarrow[EtOH]{\text{STEP 1 NaOEt}} A \xrightarrow[\text{ii. } \Delta]{\text{STEP 2 i. NaOH, } H_2O} B$$

IFoS 2021 · Q6(a) Malonic ester ring synthesis; Wittig olefination [10 marks]

(i) Complete the following reaction and give appropriate mechanism (with proper arrows and charges): 5

$$H_2C(CO_2Et)_2 + Br-CH_2CH_2CH_2-Br \xrightarrow[\text{(ii) Hydrolysis, } \Delta]{\text{(i) NaOEt}} ?$$

(ii) Complete the following reaction and give suitable mechanism to justify the geometry of the major product: 5

$$PhCHO + CH_3CH_2CH_2-\overset{\oplus}{P}Ph_3\ \overset{\ominus}{Cl} \xrightarrow{KOBu^t} ?$$

IFoS 2021 · Q6(c)(i) Cyclization of a beta-hydroxy phenethylamide [5 marks]

(i) Identify the products (A) and (B) in the following reaction sequence and give appropriate mechanism (with proper charges and arrows): 5

$$PhCH(OH)CH_2NH_2 \xrightarrow{\text{1 equiv. of } (H_3CCO)_2O} A \xrightarrow{POCl_3} B$$

IFoS 2021 · Q6(d) Fischer indole synthesis [5 marks]

Write a method for synthesis of indole where [3,3]-sigmatropic rearrangement is one of the key steps.

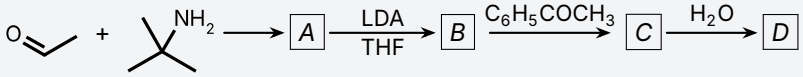
2020

CSE 2020 · Q1(d) Why Grignard reactions cannot occur in cells [10 marks]

Although carbon and magnesium are both common elements in the human body, Grignard reactions do not occur in cells. Why is it so?

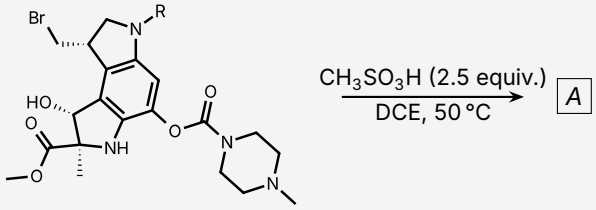
CSE 2020 · Q2(c) Directed aldol reaction through an aza-enolate [20 marks]

Complete the following reaction sequence by identifying the missing intermediates/products/reagents as the case may be. Explain the chemistry of each step by writing detailed mechanism involved. Also identify the name reaction involved:



CSE 2020 · Q4(a) Acid-catalysed Wagner–Meerwein aromatisation (duocarmycin B2 unit) [15 marks]

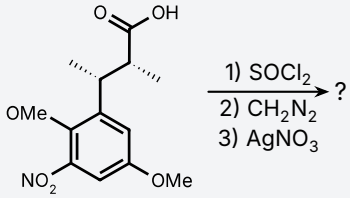
Identify the product and the name reaction involved in the following conversion. Also write the mechanism involved offering suitable explanation for the choice of CH_3SO_3H for this reaction:



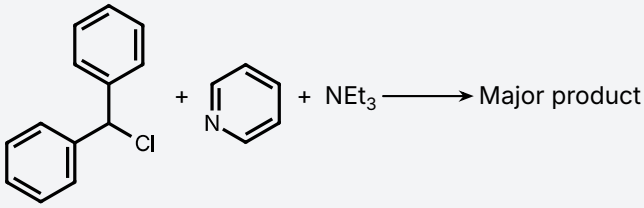
DCE = Dichloroethane

CSE 2020 · Q4(c) Arndt–Eistert homologation; SN1 capture by pyridine [20 marks]

(i) Identify the product and briefly discuss the steps involved in the following reaction:



(ii) The rate constant for the reaction of diphenylchloromethane with pyridine and triethylamine is same. Write the structure of the major product in the following reaction. Justify your answer:



(1 : 1, large excess)

IFoS 2020 · Q1(h) Mixed benzoin: p-nitrobenzaldehyde with benzaldehyde and NaCN [5 marks]

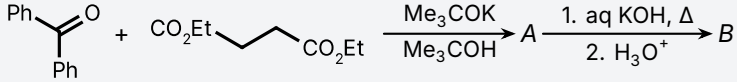
Write, why *p*-nitrobenzaldehyde does not react with sodium cyanide but a mixture of *p*-nitrobenzaldehyde and benzaldehyde reacts with this reagent. What is the name of this reaction?

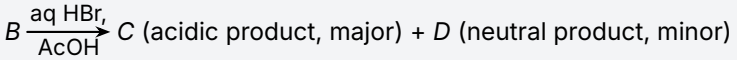
IFoS 2020 · Q2(c) Favorskii: D incorporated from 2-bromocyclohexanone but not 2-bromocyclobutanone [15 marks]

When each of 2-bromocyclohexanone (*A*) and 2-bromocyclobutanone (*B*) is reacted with EtO^-/EtOD, D is incorporated in the ring of the product/s obtained from *A* but not in that obtained from *B*. Mechanistically justify these observations.

IFoS 2020 · Q3(d) Stobbe condensation of benzophenone (A–D) [10 marks]

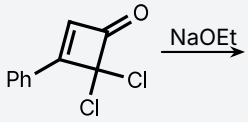
Predict the products (*A* to *D*) for the following reaction steps and name the reaction of the first step.





IFoS 2020 · Q3(e) Ring contraction of a dichlorocyclobutanone; ortho-hydroxylation of a phenol [5 marks]

(i) Predict the product showing mechanism of the following reaction:



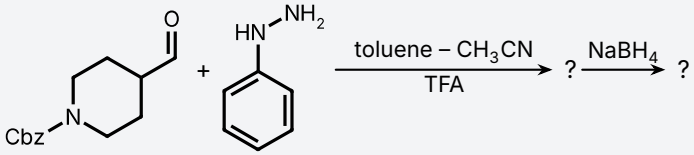
(ii) Write the appropriate reagent to be used for the following one-step conversion:



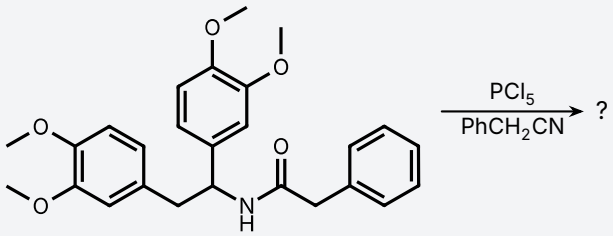
IFoS 2020 · Q4(a) Fischer indole/reduction, Bischler–Napieralski and Doebner–Miller reactions [15 marks]

Formulate the product(s) and mechanism of the following reactions:

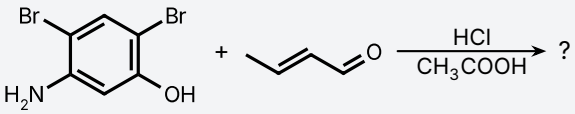
(i)



(ii)

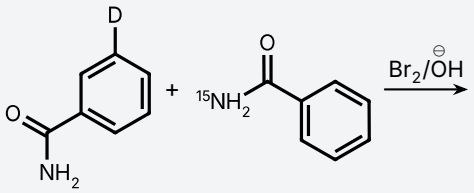


(iii)



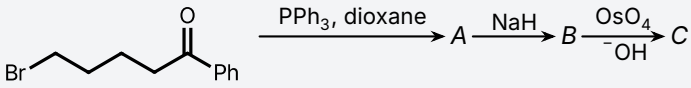
IFoS 2020 · Q4(e) Hofmann crossover with D- and ^{15}N-labelled benzamides [4 marks]

Predict the products of the following reaction showing proper distribution of D and ^{15}N in each of these.



IFoS 2020 · Q6(d) Intramolecular Wittig then OsO_4 (A–C) [10 marks]

Draw the structure of the product(s) obtained in each step of the following reactions depicting also the intermediates of the second step. Show the relative stereochemistry of the attached group in the final product. Name the reaction involved in the first two steps.



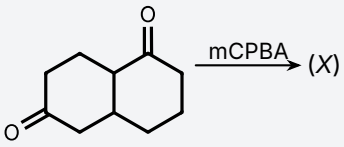
2019

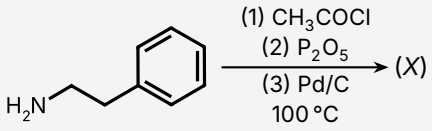
CSE 2019 · Q1(c) Neopentyl tosylate: 1,2-methyl shift [10 marks]

Neopentyl tosylate on solvolysis gives 2-methylbutan-2-ol. Write the mechanism of its formation.

CSE 2019 · Q1(d) Baeyer–Villiger oxidation; Bischler–Napieralski synthesis [10 marks]

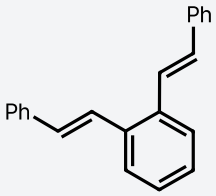
Identify the product (*X*) in the following reactions and write the name of the reaction involved:

(i) 

(ii) 

CSE 2019 · Q2(b) 1,2-Distyrylbenzene from phthalic acid by Wittig reaction [15 marks]

Outline the synthesis of the following compound using Wittig reaction starting with phthalic acid:



CSE 2019 · Q2(c) Dehydration of 3,3-dimethylbutan-2-ol: methyl shift and Saytzeff alkene [20 marks]

Write different olefins expected to be formed in the following dehydration reaction:

$$(CH_3)_3CCHOHCH_3 \xrightarrow[\Delta]{H_2SO_4}$$

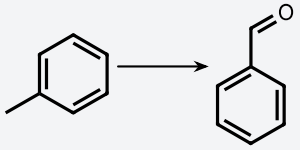
Provide a mechanism for their formation. Which product is expected to be most stable?

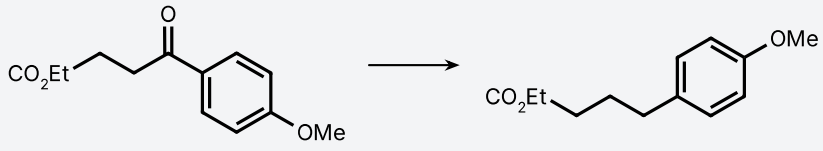
CSE 2019 · Q3(c) Fischer indole synthesis with butan-2-one: two indoles [20 marks]

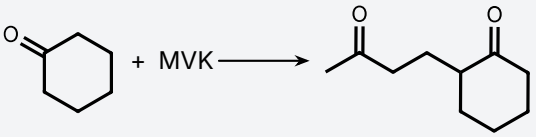
In Fischer indole synthesis, phenylhydrazine upon reaction with 2-butanone in presence of PPA, gives a mixture of two indoles in equimolar ratio. Predict their structures and explain their formation.

CSE 2019 · Q4(b) 'Etard reaction, Clemmensen reduction, Michael addition [15 marks]

Write the name of the reaction and reagent required for the following conversions:

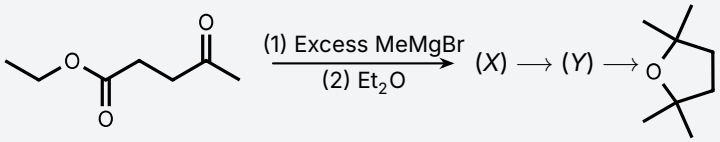
(i) 

(ii) 

(iii) 

CSE 2019 · Q4(c)(i) Ethyl levulinate with excess methylmagnesium bromide [10 marks]

Predict the structure of (*X*) and (*Y*) in the following sequence:

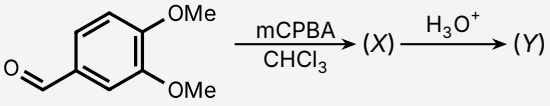


CSE 2019 · Q4(c)(ii) Reimer–Tiemann reaction of p-cresol: normal and abnormal products [10 marks]

p-methylphenol on reaction with $OH^-/CHCl_3$ gives two products. Write the structure of both and propose a suitable mechanism.

CSE 2019 · Q5(b) Baeyer–Villiger oxidation of an electron-rich aldehyde [10 marks]

Identify (*X*) and (*Y*) in the following reaction and outline the mechanism for the formation of (*X*):



CSE 2019 · Q6(c) Nylon-6 from cyclohexanone: Beckmann rearrangement [20 marks]

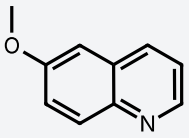
How can Nylon-6 be prepared from cyclohexanone? What is the name of the monomer of Nylon-6? Write the mechanism of the reaction and name the reaction involved.

IFoS 2019 · Q1(a) Cannizzaro reaction: where the second hydrogen comes from [5 marks]

In the Cannizzaro reaction of benzaldehyde, suggest a suitable method to know the source of second hydrogen that becomes attached to benzyl alcohol, i.e., if it comes from solvent (H_2O) or from a second molecule of benzaldehyde.

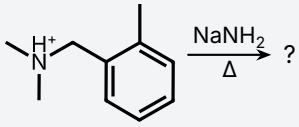
IFoS 2019 · Q1(f) Skraup synthesis of 6-methoxyquinoline [5 marks]

How will you prepare the following compound by Skraup synthesis? Give mechanism for its formation:



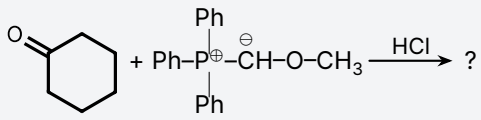
IFoS 2019 · Q1(g) Sommelet–Hauser rearrangement with $NaNH_2$ [5 marks]

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



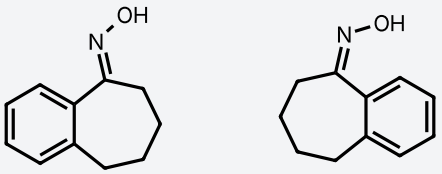
IFoS 2019 · Q1(h) Wittig with a methoxymethylene ylide, then HCl: homologation to an aldehyde [5 marks]

Give the product and mechanism of the following reaction:



IFoS 2019 · Q2(d) Beckmann rearrangement of two benzosuberone oxime isomers with PCl_5 [10 marks]

Comment if the following two compounds will yield same product or different products on treatment with PCl_5. Explain:



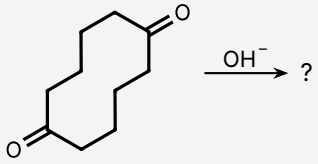
IFoS 2019 · Q3(a) pKa of 1,3-dicarbonyls; intramolecular aldol of cyclodecane-1,6-dione [10 marks]

(i) Arrange the following compounds in increasing order of their pK_a values. Justify your answer:

1. $CH_2(COMe)_2$
2. $CH_2(CO_2Et)_2$
3. $MeCOCH_2CO_2Et$

5

(ii) Complete the following reaction:

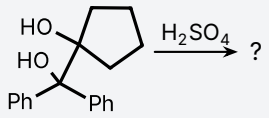


5

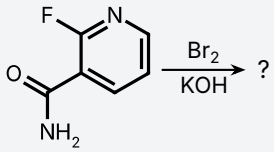
IFoS 2019 · Q3(c) Pinacol rearrangement of a cyclopentyl diol; Hofmann degradation of a fluoronicotinamide [10 marks]

Identify the products and briefly describe the steps involved: 5×2=10

(i)



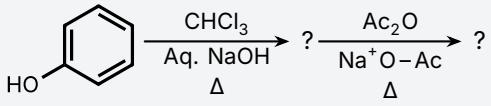
(ii)



IFoS 2019 · Q4(a) Reimer–Tiemann then Perkin; Claisen condensation of ethyl acetate [10 marks]

Formulate the product(s) and give the mechanism for the following reactions: 5×2=10

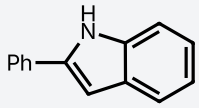
(i)

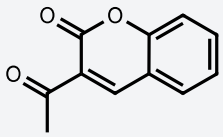


(ii) $2CH_3COOC_2H_5 \xrightarrow[EtOH]{EtO^-} ?$

IFoS 2019 · Q4(b) Fischer indole route to 2-phenylindole; Knoevenagel route to 3-acetylcoumarin [10 marks]

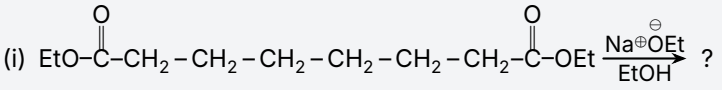
Suggest starting materials and conditions to prepare the following molecules based on Fischer indole and Knoevenagel condensation reactions:

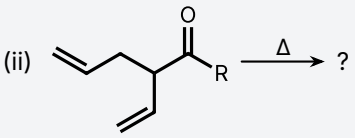
(i) 

(ii) 

IFoS 2019 · Q4(c) Dieckmann condensation; Claisen rearrangement of an allyl aryl ketone ether [10 marks]

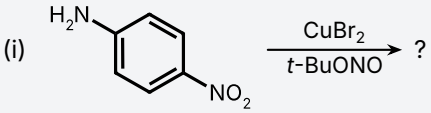
Formulate the products and mechanism of the following reactions:

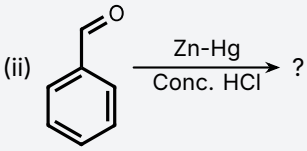
(i) 

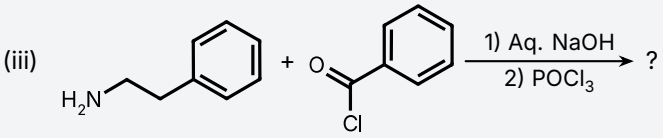
(ii) 

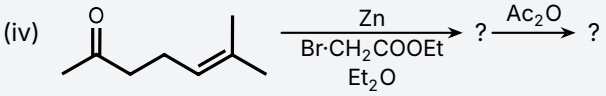
IFoS 2019 · Q4(d) Sandmeyer-type, Clemmensen, Schotten–Baumann/$POCl_3$ and Reformatsky products [10 marks]

Write the structures of the products of the following reactions:

(i) 

(ii) 

(iii) 

(iv) 

2018

CSE 2018 · Q3(b) Skraup synthesis of 8-methylquinoline; Fries rearrangement [10 marks]

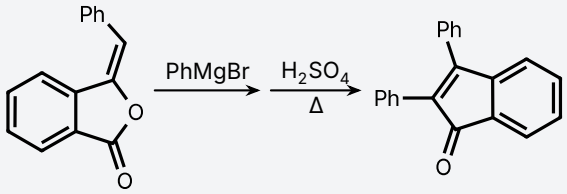
Answer the following briefly :

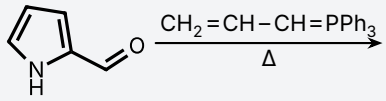
(i) How can you prepare 8-methylquinoline starting with *o*-toluidine as one of the starting materials?

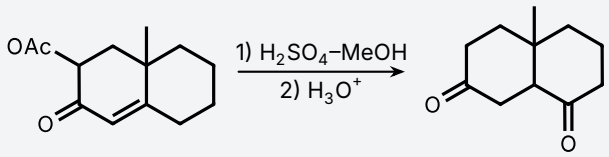
(ii) With suitable example, comment whether Fries rearrangement proceeds intermolecularly or intramolecularly. Give evidence in favour of your answer.

CSE 2018 · Q3(c) Indenone, Wittig and octalone mechanisms [15 marks]

Write the mechanism of the following :

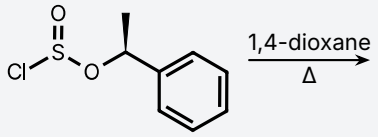
(i) 

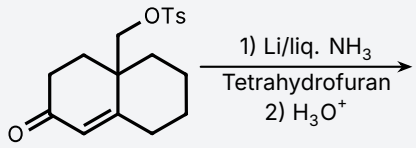
(ii) 

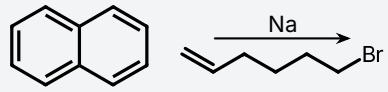
(iii) 

CSE 2018 · Q3(d) $SOCl_2$/dioxane, Li/NH_3 cyclisation, sodium naphthalenide [15 marks]

Predict the product(s) with mechanism for the following :

(i) 

(ii) 

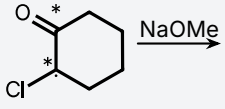
(iii) 

CSE 2018 · Q5(a) Favorskii rearrangement: one product from two chloroketones [10 marks]

Each of $PhCH_2COCH_2Cl$ and $PhCHClCOCH_3$ in reaction with NaOMe/MeOH furnishes the same product. What mechanistic implication can be drawn from the above fact?

IFoS 2018 · Q1(d) Favorskii rearrangement of ^{14}C-labelled 2-chlorocyclohexanone [5 marks]

Predict the products of the following reaction showing distribution of the labelled carbon (∗ = ^{14}C) and the mechanism:



IFoS 2018 · Q2(b) Aldol of methyl ketones: methyl attack with base, methylene with acid [5 marks]

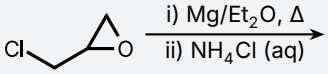
Explain why methyl alkyl ketones (RCH_2COCH_3) undergo aldol condensation via attack at the methyl group in the presence of base catalyst, but via attack at the methylene group in the presence of acid catalyst.

IFoS 2018 · Q3(a) Mixed benzoin condensation of p-dimethylaminobenzaldehyde [5 marks]

Discuss why *p*-dimethylaminobenzaldehyde does not undergo any reaction with KCN, but a mixture of this and benzaldehyde does, giving a condensation product. Name the reaction also.

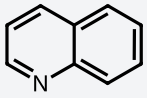
IFoS 2018 · Q3(b) Epichlorohydrin with Mg: product and mechanism [5 marks]

Predict the product and draw the probable mechanistic pathway of the following reaction:



IFoS 2018 · Q4(c) Skraup synthesis of quinoline; pentaerythritol from HCHO [10 marks]

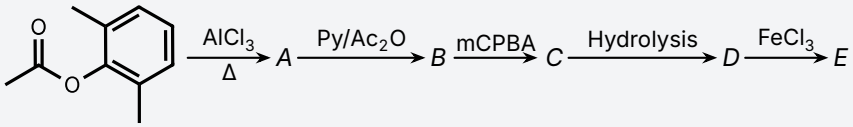
Carry out the following transformations: 5×2=10

(i) Glycerol ⟶ 

(ii) HCHO ⟶ $C(CH_2OH)_4$

IFoS 2018 · Q4(d) Fries rearrangement then Dakin-type oxidation (A–E) [10 marks]

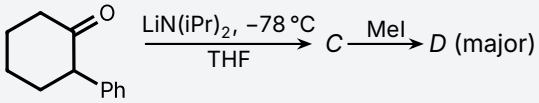
Write the structure of the products (*A* to *E*) in each step of the following sequence of reactions:



2017

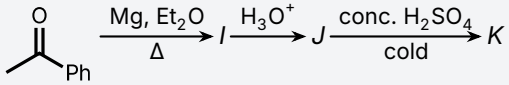
CSE 2017 · Q1(d) LDA at -78°C: kinetic enolate of 2-phenylcyclohexanone [10 marks]

Give the structures of C and D and account for their formation.



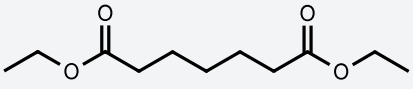
CSE 2017 · Q2(c) Acetophenone pinacol and the pinacol–pinacolone rearrangement [15 marks]

Write the structures of *I* to *K*. The conversions mentioned below involve a rearrangement at one step. Name it and depict the corresponding mechanism.



CSE 2017 · Q2(d) Bouveault–Blanc reduction and acyloin condensation [15 marks]

Predict the product in each of the following reactions and write the mechanism for each conversion.



upper path: excess Na, EtOH, reflux

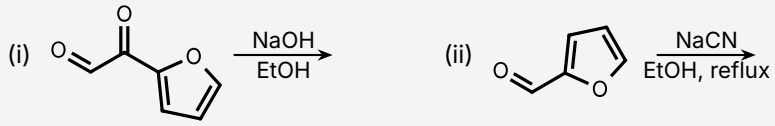
lower path: (i) Na, xylene, reflux; (ii) H_2O

CSE 2017 · Q3(a) Acetylacetone with MeMgI; conversion to hexane-2,4-dione [10 marks]

What happens when 2,4-pentadione is treated with one equivalent of MeMgI? How can you convert the mentioned dione to 2,4-hexadione?

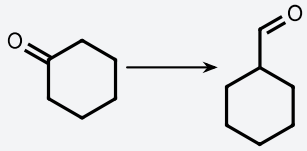
CSE 2017 · Q3(d) Intramolecular Cannizzaro of furylglyoxal; furoin [10 marks]

Write the structure of the product(s) for each of the following transformations and write the name of each reaction.



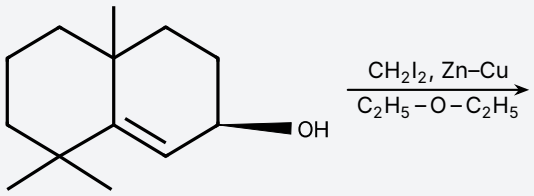
CSE 2017 · Q5(b) Cyclohexanone to cyclohexanecarbaldehyde in two steps [10 marks]

How will you convert the following reactant into product by a two-step process? Also give the mechanism.



CSE 2017 · Q5(c) Simmons–Smith reaction directed by an allylic OH [10 marks]

Write the product for the following reaction and give the mechanism along with type of addition at the >C=C< bond.

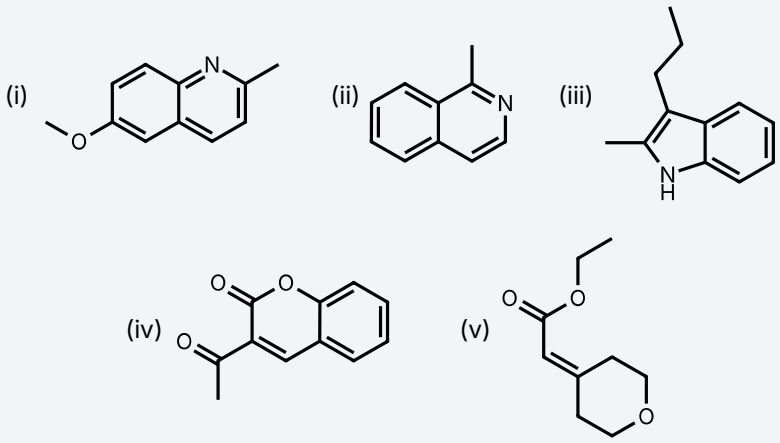


CSE 2017 · Q5(d) Regiospecific reaction; aniline to p-phenylenediamine [10 marks]

Define a regio specific reaction. How will you convert aniline into p-phenylene diamine?

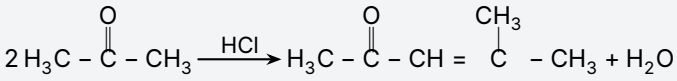
CSE 2017 · Q8(a) Starting compounds for five heterocycles [10 marks]

Suggest suitable starting compounds and structures for the synthesis of the following heterocyclic compounds.



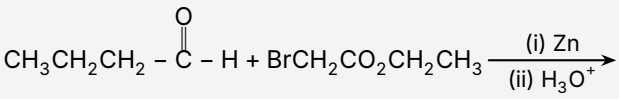
IFoS 2017 · Q1(d) Acid-catalysed self-condensation of acetone to mesityl oxide [5 marks]

Show the mechanism for the following reaction:



IFoS 2017 · Q1(e) Reformatsky reaction of butanal [5 marks]

Mention the product in the given reaction:



Also provide mechanism of the above reaction.

IFoS 2017 · Q1(f) Pinacol to pinacolone [5 marks]

How 2,3-dimethyl-2,3-butanediol can be converted to 3,3-dimethyl-2-butanone? Suggest the mechanism of the involved reaction.

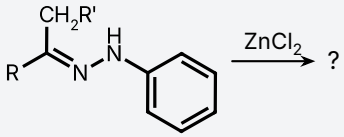
IFoS 2017 · Q2(c) Hofmann rearrangement of benzamide; $LiAlH_4$ and C=C bonds [10 marks]

(i) Give the mechanistic steps for the synthesis of aniline from benzamide. 5

(ii) Why does $LiAlH_4$ usually fail to reduce a C–C multiple bond? Why does such a bond in conjugation with an aromatic system on one side and a carbonyl group on the other side get reduced by $LiAlH_4$? 5

IFoS 2017 · Q4(a) Fischer indole synthesis [10 marks]

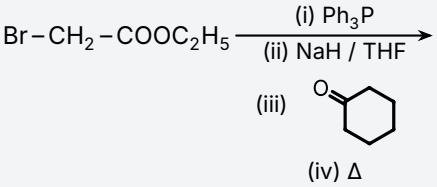
Mention the product(s) in the following reaction. Suggest the mechanism of this reaction. What is the popular name of this reaction?



[R′, R = alkyl, aryl or hydrogen]

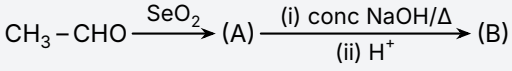
IFoS 2017 · Q8(d) Wittig with cyclohexanone; aldol then SeO_2 oxidation [10 marks]

(i) Complete the given reaction and give its mechanism:



5

(ii) Complete the following reaction sequence and give mechanism for the formation of (B) into (C):



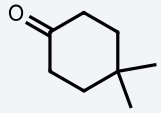
5

2016

CSE 2016 · Q2(d) Skraup synthesis; Wolff–Kishner reduction [10 marks]

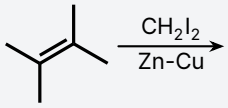
Identify (*X*) in the reactions given below:

(i) $C_6H_5NH_2 + C_6H_5NO_2 + (X) \xrightarrow[\Delta]{H_2SO_4/FeSO_4}$ Quinoline

(ii)  $\xrightarrow[OH^-]{NH_2NH_2}$ (*X*)

CSE 2016 · Q3(c) Simmons–Smith; $SOCl_2$ on crotyl alcohol; Beckmann rearrangement [30 marks]

Predict the major products in the following reactions and write the mechanism:

(i) 

(ii) $H_3C-CH=CH-CH_2OH \xrightarrow{SOCl_2}$

(iii) $C_6H_5-C(CH_3)=O \xrightarrow[2)\ PCl_5]{1)\ NH_2OH}$

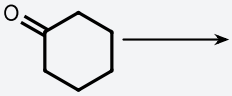
CSE 2016 · Q4(a) Stobbe condensation; Fries rearrangement [15 marks]

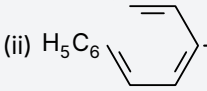
(i) Stobbe condensation of acetophenone with succinic acid gives two products. Write their structure and stereochemistry.

(ii) Phenyl acetate reacts with $AlCl_3$ in an inert solvent to give two isomers. Write their structures and indicate how you will separate them.

CSE 2016 · Q4(d) Cyclohexanone to nylon-6; phenylhexatriene to biphenyl [15 marks]

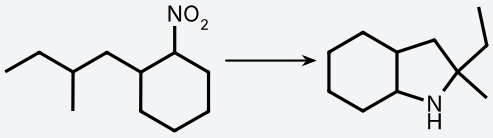
Write various steps for the following conversions:

(i)  Nylon-6

(ii)  Biphenyl

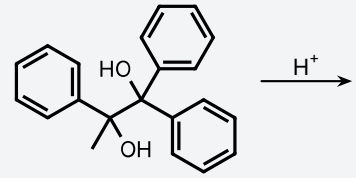
CSE 2016 · Q5(c) Pyrrolidine ring by the Hofmann–Löffler–Freytag reaction [10 marks]

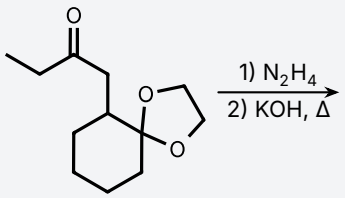
How will you carry out the following conversion? Write the steps involved in it:



CSE 2016 · Q7(a) Pinacol rearrangement; Wolff–Kishner beside a ketal [15 marks]

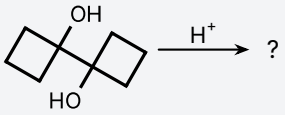
Identify the major products in the following reactions and discuss their formation:

(i) 

(ii) 

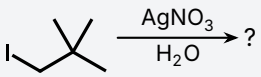
IFoS 2016 · Q1(h) Pinacol rearrangement with ring expansion [5 marks]

Write the product and mechanism of the reaction :



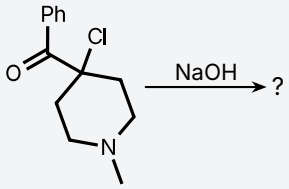
IFoS 2016 · Q3(a)(i) Neopentyl iodide with aqueous silver nitrate: 1,2-methyl shift [5 marks]

Write the structure of the product formed.



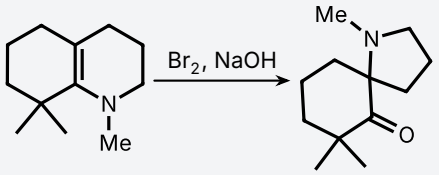
IFoS 2016 · Q3(a)(ii) An α-chloro ketone without α′-H: quasi-Favorskii rearrangement [5 marks]

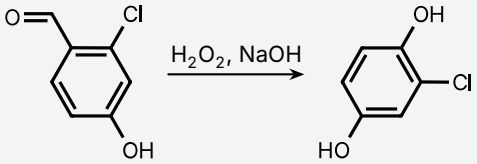
Write the structure of the product formed.



IFoS 2016 · Q4(a) Enamine bromination with ring contraction; Dakin reaction [10 marks]

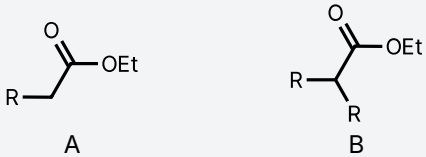
Suggest a mechanism for the following reactions :

(i) 

(ii) 

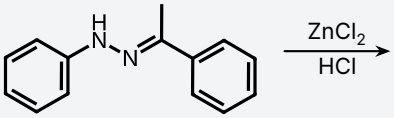
IFoS 2016 · Q4(b) Claisen ester condensation: why R_2CHCO_2Et fails [10 marks]

Claisen-ester condensation is possible with substrates of type A but not possible with type B. Explain by writing the mechanism.



IFoS 2016 · Q4(c) Fischer indole synthesis: 2-phenylindole [10 marks]

Discuss the mechanism of the reaction by writing the product.



IFoS 2016 · Q4(d) Stabilised and unstabilised ylids; E/Z selectivity in the Wittig reaction [10 marks]

What are stabilized and unstabilized ylids ? How does E-Z selectivity in Wittig reaction depend upon the nature of ylid ? Explain.

IFoS 2016 · Q8(b)(ii) Baeyer–Villiger oxidation of camphor [5 marks]

Identify the X.

