End - Semester Exam

Time: 2.5 h 27 April 2023

# Answer Part A and Part B (Main Answer Sheet) separately Part A (15 Marks)

[2-(methylamino)-1-phenylpropan-1-ol]

Label the faces of the functional group in the following compounds as homotopic, enantiotopic, or diastereotopic. Demonstrate by any suitable reaction. (2+2 marks)

- Calculate the ee and the specific rotation of a mixture containing 10 g of (+)-2-butanol and 6 g of (-)-2-butanol. The specific rotation of enantiomerically pure (+)-2-butanol is +13.5°.
   (2.5 marks)
- Label the following pairs of structures as homomers, enantiomers, diastereoisomers, or constitutional isomers. Justify. (1.5+1.5 = 3 marks)

 Indicate the marked hydrogens Ha and Hb as of what topicity? Provide replacement test. (1.5 marks)

#### Part B (Main Answer Sheet) (35 Marks)

 Identify and explain the formation of the major products with the right models in the following reactions.
 (2.5 + 2.5 = 5 marks)

a. 
$$\frac{Br_2}{Cl} = A \xrightarrow{NaOMe} B$$
 b.  $\frac{Me_2Cuti}{ZnCl_2} \xrightarrow{?} Cl \xrightarrow{ZnCl_2} \frac{Me_2Cuti}{ZnCl_2} \xrightarrow{?} Cl \xrightarrow{Re_2Cuti} \frac{Re_2Cuti}{ZnCl_2} \xrightarrow{?} Cl \xrightarrow{Re_2Cuti} \frac{Re_2Cuti}{ZnCl_2} \xrightarrow{?} Cl \xrightarrow{Re_2Cuti} \frac{Re_2Cuti}{ZnCl_2} \xrightarrow{?} Cl \xrightarrow{Re_2Cuti} \frac{Re_2Cuti}{ZnCl_2} \xrightarrow{Re_2Cuti} \frac{Re_2Cuti}{ZnCl_2}$ 

 Derive the major diastereomer formation in the following reduction reaction with the appropriate TS model. (2.5 + 2.5 = 5 marks)

 Derive the major diastereomer formation in the following reduction reaction using the correct transition state model. (2.5 + 2.5 = 5 marks)

 Derive the main diastereomer formation in the following reaction using the suitable conformation/model. (5 marks)

## Organic Chemistry II (CH3202) Department of Chemical Sciences, HSER Kolkata

Total marks: 15 + 35 = 50 marks

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 Explain the major diastereomer formation in the following reaction with the right conformation and TS model. (4 + 1 = 5 marks)

11. In the following acetolysis reactions, identify the products and comment on which diastereomer is undergoing faster acetolysis and the optical purity of the products.

$$(2.5 + 2.5 = 5 \text{ marks})$$

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12. Identify the products with the right stereochemistry.

$$(2+3=5 \text{ marks})$$

### (Attempt all)

- Find out the absolute configuration of the chiral centre of the product (show the structure) obtained from the nucleophilic attack on the Re face of benzaldehyde by MeMgl.
   (3.0 marks)
- Cis isomer of 4-hydoxycyclohexane-1-carboxylic acid undergoes intramolecular esterification on simple heating while the transisomer does not. Explain.
   (3.0 marks)

3. Which isomer (cis or trans) of the following compound (4-t-butylcyclohexanol) will undergo oxidation with chromic acid at a faster rate and why? Is the rate-determining step important for your answer, show mechanistically? (0.5+3.0 marks)

Among the two isomers (E vs Z) of the following molecule, which one would have more contribution from the conformation where methyl is in axial position? Explain. (0.5+2.0 marks)

5. Comment whether this statement is true or false "In some cases, conformational isomers can be isolated in room temperature". Justify with an example (chemical structure). (0.5+1.5 marks)



- Explain why the ratio of H-bonded to unbonded -OH is higher for the optically active isomer of butane-2,3-diol [CH3-CH(OH)-CH3] than for the meso isomer.
- Between cis and trans isomers of 1,2 dimethyl cyclohexane, one isomer is more stable than the other by a ~ 1.8 kcal mole<sup>-1</sup>.
   Explain considering gauche butane interactions. What would be your answer, if you compare cis 1,2 dimethyl cyclohexane and 1,2 dimethyl cyclohexane with both methyls in axial positions.
- Indicate the topicity of the marked protons with justification from replacement test.

(0.5+1.5)x2=4 marks

a) 
$$CF_3$$
  $H$   $CH_3$   $CI$   $C=C=C$ 

9. What is the stereochemical relationship (homomer, constitutional isomer, diastereoisomer or enantiomers) between the following pairs of the structures.? (0.5+1.5)x2=4 marks)

(a) 
$$CH_2CI$$
  $CH_2CI$   $CH_2CI$   $CH_2CH_3$   $CH_2CH_3$ 

# Answer Part A and Part B separately Part A (15 Marks)

- 1. The ketone (+)-CH<sub>3</sub>CH<sub>2</sub>COCH(OII)CII<sub>3</sub> racemizes on treatment with alkali, whereas the isomeric ketone (+)-CII<sub>3</sub>COCH<sub>3</sub>CH(OH)CH<sub>3</sub> does not. Explain the observation (1 marks)
- Q2. Indicate the topicity of the marked protons. (1 marks)

Q3. Optical active camphene (shown below) undergoes racemization on treatment with acid. Explain the observation. (2 marks)

Q4. Label the following pair of Structures as homomers, constitutional isomers, diastereomers or enantiomers. (1.5 marks)

Q5. Label the carbonyl faces in the following compounds as homotopic, enantiotopic or diasteroteopic. Demonstrate by a suitable reaction. (2 + 2 = 4 marks)

Q6. Label the following pairs of structures as homomers, enantiomers or diastereoisomers. (1 + 1 = 2 marks)

Explain with proper structures and mechanism the following observation. (1.5 marks)

Q8. Draw the more stable conformation for each of the following compounds (1 + 1 = 2 marks)

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Total marks: 15+35=50 marks

# Part B (35 Marks)

Q9. Identify and explain the formation of the major product in the following

Q10. Find out major diastercomer formation in the following reduction reaction with the appropriate TS model. (2.5 + 2.5 = 5 marks)

Q11. Derive the main diastercomer formation in the following reactions with appropriate stereochemistry and conformation. (2.5 + 2.5 = 5 marks)

Q12. Derive the main diastereomer formation in the following allylation reaction using the right model. (2.5 + 2.5 = 5 marks)

Q13. Explain the main enolate formation in the following reaction using the appropriate transition state model. (2.5 + 2.5 = 5 marks)

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Q14. Derive the main diastereomer formed in the following reduction reaction using the right transition state model. (2.5 + 2.5 = 5 marks)

Q15. Elaborate on the main diastereomer formation in the following NaBH. reduction reactions with the right model. (2.5 + 2.5 = 5 marks)

? 
$$\frac{NaBH_4}{R = OH}$$
  $\frac{NaBH_4}{R = CO_2Me}$  ?

## Mid Sem Exam: CH3202 Full Marks 30 (Attempt all)

Label the following pairs of structures as homomers, constitutional isomers, enantiomers or diastereomers. Show support of your answers (1.5 x 4=6 marks)

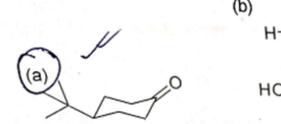
(a) 
$$H_3C \stackrel{H}{\longrightarrow} O$$
  $O$   $CH_3$   $H_3CH_2C$   $CH_2CI$   $CH_2CI$   $CH_2CI$   $CH_2CI$   $CH_2CI$   $CH_3CH_3$   $CH_3CH_3$   $CH_3CH_3$   $CH_3CH_3$   $CH_3CH_4$   $CH_3CH_5$   $CH_4CH_5$   $CH_5$   $CH_$ 

2. Predict with scheme how the following racemic pair of alcohols can be separated with the help of pthalic anhydride, pyridine and enantiopure morphine. (3 marks)

Draw the chair conformations of cis and trans decalin and justify why flipping is possible for only one (either cis or trans) isomers. (2+3 marks)

# Mid Sem Exam: CH3202 Full Marks 30 (Attempt all)

4. Label the C=O faces (of a, b) and the labelled protons (c,d) in each of the following compounds in terms of topicity. Demonstrate by suitable reactions. (2x4=8 marks)



Assign the configuration (R, S) of the starting material and suggest whether the relative configuration is retained or inverted (No explanations). (1+1 marks)

\$.

Draw the structure of two diastereoisomers having the configuration (2S,3R) and (2S,2S) of ethyl 2-methyl-3-hydroxy-3-phenylpropanoate. Assign these isomers as erythro- and threo- form? How can you predict the most stable preferred conformations of only the threo isomer. (1.5+1.5+1 +2 marks)

### Organic Chemistry II (CH3202) Department of Chemical Sciences, IISER Kolkata Total marks: 15 + 35 = 50 marks

Time: 2.5 h

11 May 2024

# Answer Part A and Part B Separately Part A (Supplementary Answer Sheet) (15 Marks)

1. Account for the following observations

$$(1.5 + 3 = 4.5 \text{ marks})$$

Which one of the following alcohols (I and II) is expected to form an epoxide on treatment with a base and why? (2.5 marks)

The erythro isomer of 1-bromo-1,2-diphenyl propane (BrCHPh-CHPhMe) undergoes base induced dehydrobromination at a much slower rate than the threo isomer. Explain the observations mechanistically and with the help of (4 marks) conformations.

Find out the absolute configuration of the chiral centres of the products for the following reactions, when

benzaldehyde undergoes nucleophilic attack by MeMgl on the Re-face.

Br2 is added to the Re-Re and Si-Si faces of malcic acid (trans addition of (1+3=4 marks)bromine)

## Part B (Main Answer Sheet) (35 Marks)

Draw the catalytic cycle and explain the formation of the major product in the following reactions.

Find the major diastereomer formation in the following reduction reaction with the (1+1=2 marks)mechanism.

7. Derive the major diastereomer formation in the following reaction and draw the (2+1+1=4 marks)conformation of the starting compound and the product.

Explain the main diastereomer formation in the following reaction using the suitable (2 mark conformation/intermediate/TS model.

9. Explain the major diastereomer formation in the following reaction with the rig (1+1=2 mar conformation and TS model.

### Organic Chemistry II (CH3202)

### Department of Chemical Sciences, IISER Kolkata

Total marks: 15 + 35 = 50 marks

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to In the following acetolysis reactions, identify the products and comment on which diastereomer is undergoing faster acetolysis and the optical purity of the products.

11/Identify the product with the right stereochemistry and mechanism. (3 marks)

12. Explain why the following cyclic amine undergoes racemization during resolution.
(2 marks)

Explain the diastereomeric ratio observed in the following reactions using the suitable conformation/TS model. (2+2=4 marks)

14. Find out the intermediate in the following reaction and explain the formation of a major diastereomeric product with suitable TS (1+2=3 marks)

15 Elaborate on the main diastereomer formation in the following NaBH reduced teactions with the suitable model. (2 + 2 = 4 marks)

MidSem Exam: CH3202

attack on the Re face of benzaldehyde by MeMgl.

(Attempt all)

(3.0 marks)

- Find out the absolute configuration of the chiral centre of the product (show the structure) obtained from the nucleophilic
- Cis isomer of 4-hydoxycyclohexane-1-carboxylic acid undergoes intramolecular esterification on simple heating while the transisomer does not. Explain. (3.0 marks)

Which isomer (cis or trans) of the following compound (4-t-butylcyclohexanol) will undergo oxidation with chromic acid at a
faster rate and why? Is the rate-determining step important for your answer, show mechanistically? (0.5+3.0 marks)

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 Comment whether this statement is true or false "In some cases, conformational isomers can be isolated in room temperature". Justify with an example (chemical structure). (0.5+1.5 marks)



### (Attempt all)

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   Explain considering gauche butane interactions. What would be your answer, if you compare cis 1,2 dimethyl cyclohexane and 1,2 dimethyl cyclohexane with both methyls in axial positions. {2.5+2.5 marks}
- 8. Indicate the topicity of the marked protons with justification from replacement test.

(0.5+1.5)x2=4 marks

9. What is the stereochemical relationship (homomer, constitutional isomer, diastereoisomer or enantiomers) between the following pairs of the structures.? (0.5+1.5)x2=4 marks)

(a) 
$$CH_2CI$$
  $CH_2CI$   $CH_2CI$  (b)  $CH_3CH_3$   $CH_2CH_3$   $CH_2CH_3$   $CH_3C$   $CH_2CH_3$   $CH_3C$   $CH_2CH_3$   $CH_3C$   $CH_3$   $CH_3$