

# WEST BENGAL STATE UNIVERSITY

B.Sc. Honours 3rd Semester Examination, 2020, held in 2021



# CEMACOR07T-CHEMISTRY (CC7)

## **ORGANIC CHEMISTRY-III**

Time Allotted: 2 Hours Full Marks: 40

The figures in the margin indicate full marks.

Candidates should answer in their own words and adhere to the word limit as practicable.

All symbols are of usual significance.

# Answer any four questions taking one from each unit

## **UNIT-I**

1. (a) State whether the formation of Me <sub>3</sub> CCH(OH)Me by acid catalyzed hydration of Me <sub>3</sub> CCH=CH <sub>2</sub> is possible or not. If not, then how this transformation could be achieved?	
(b) Three isomeric alkenes A, B and C with molecular formula C <sub>5</sub> H <sub>10</sub> on hydrogenatic produce 2-methylbutane. A and B give the same tertiary alcohol of oxymercuration-demercuration. B and C give different primary alcohols of hydroboration-oxidation. Logically deduce structures of A, B and C.	on
(c) Carry out the following conversions:	2+2
(i) 2-butyne to ( <i>Z</i> )-2,3-dideutero-2-butene	
(ii) 4, 4-dimethyl-2-pentene to 4, 4-dimethyl-1-pentene.	
2. (a) Singlet carbene adds to <i>cis</i> -2-butene in a stereospecific manner whereas triple carbene does not — Explain.	et 3
(b) Identify the product(s) formed when 1-octene is reacted with NBS/CCl <sub>4</sub> . Predict the relative yields with proper justification.	ne 2
(c) What happens when 1, 3-butadiene is treated with HBr at $-80^{\circ}$ C and at $40^{\circ}$ separately? Predict the product composition in each case and offer proper explanation in support of your answer.	
(d) Give a simple reaction to distinguish 1-butyne from 2-butyne.	1
(e) Write structural formula for the compound which yields pentane-1,5-dial or reductive ozonolysis.	on 1

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#### **UNIT-II**

- 3. (a) Pivaloyl chloride (Me<sub>3</sub>CCOCl) reacts with benzene in presence of anhydrous AlCl<sub>3</sub> to give mainly tert-butylbenzene whereas anisole under same reaction condition gives mainly *p*-methoxypivalophenone Explain.
  - 2.

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- (b) Predict the favoured position of aromatic electrophilic substitution of the following compounds and justify your answer in each case:
  - (i) Ph-CH=CH-CO<sub>2</sub>H
- (ii) Ph-CO<sub>2</sub>H
- (c) Compare reactivity of PhNHCOCH<sub>3</sub>, aniline and benzene toward bromination reaction with proper justification. What is the major monosubstituted product formed during bromination of PhNHCOCH<sub>3</sub>?

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4. (a) Compare the reactivity of the following compounds towards nitration reaction using a mixture of concentrated  $HNO_3$  and  $H_2SO_4$ :

$$C_6H_6$$
,  $C_6D_6$ ,  $C_6H_5$ – $NO_2$  and  $C_6H_5$ – $OMe$ 

(b) Predict the product giving proper mechanism.

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(c) Account for the following observation:

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The amination of both O-chloroanisole and m-chloroanisole yields only m-anisidine.

#### **UNIT-III**

5. (a) *p*-N,N-dimethyl aminobenzaldehyde or *p*-nitrobenzaldehyde separately on treatment with KCN/EtOH fails to give benzoin condensation reaction but a mixture of these two readily responds to the reaction. Explain the observation mechanistically.

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(b) Give structural formula and name of the product of the reaction between benzaldehyde and semicarbazide. Comment on the nucleophilicsite(s) in the semicarbazide molecule.

2

(c) Write down all the possible products from a mixed Claisen condensation with CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>COOCH<sub>3</sub> and PhCH<sub>2</sub>COOCH<sub>3</sub>.

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(d) In the following reaction sequence, identify A, B and C. Suggest suitable mechanism for the conversion from B to C.

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$$A \xrightarrow{Ac_2O / NaOAc / H^+} \xrightarrow{CO_2H} B \xrightarrow{B COcl_2 / AlCl_3} C$$

(e)  $\alpha$ ,  $\beta$ -unsaturated acid, RCH<sub>2</sub>CH=CHCO<sub>2</sub>H decarboxylates readily on heating but R<sub>3</sub>CCH=CHCO<sub>2</sub>H does not. — Why?

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(f) Carry out the following conversion applying protection / deprotection technique.

$$CO_2Et$$

- (g) Optically active PhCOCH(Et)Me is racemised on base treatment but 3 PhCOCH<sub>2</sub>CH(Et)Me does not Explain.
- 6. (a) Identify the products the following reaction.

(i) 
$$O_3 / Zn - AcOH$$
  $A \longrightarrow B \xrightarrow{H_2N-NH_2 / KOH} C$ 

(ii)

(iii) 
$$+ \text{HCHO} \xrightarrow{\text{OH7/H}_2\text{O}} \text{G + H}$$

$$\overset{*}{\text{CHO}} = \text{C}^{14}$$

(b) When the following compound is treated with NaOEt/EtOH, two isomeric compounds (A) and (B) are obtained. Give suitable mechanism for the formation of the products.

$$\begin{array}{c}
\stackrel{\circ}{\longrightarrow} & CO_2Et \\
\stackrel{\circ}{\longrightarrow} & A + B
\end{array}$$

- (c) Synthesis of 2,2,5,5-Tetramethylhex-3-ene cannot be accomplished by Witting 2 reaction Explain.
- (d) Semicarbazide hydrochloride alone does not react with a ketone to give semicarbazone but when mixed with sodium acetate it does Why? Which nitrogen is involved in the reaction and why?
- (e) Convert: 2

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2

3+3+2

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## **UNIT-IV**

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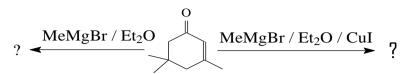
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7. (a) Give the products with proper explanations:



(b) Carry out the following conversion involving organometallic reagents:

$$(Me_2CH)_2CO \rightarrow (Me_2CH)_3COH$$

- (c) Why Zn is a specific reagent for Reformatsky reaction?
- 8. (a) Convert the following using organometallic reagents:

$$Me_2CO \rightarrow Me_2C(OH)CH_2COOH$$

- (b) What happens when PhCH<sub>2</sub>MgBr is treated with HCHO followed by acidification?
- (c) How can you prepare the acid R<sub>3</sub>C–CO<sub>2</sub>H from R<sub>3</sub>COH?

**N.B.:** Students have to complete submission of their Answer Scripts through E-mail / Whatsapp to their own respective colleges on the same day / date of examination within 1 hour after end of exam. University / College authorities will not be held responsible for wrong submission (at in proper address). Students are strongly advised not to submit multiple copies of the same answer script.

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