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 $Me_3CCH(OH)Me$ by acid catalyzed hydration of $Me_3CCH{=}CH_2$ is possible or not. If not, then how this transformation could be achieved? 3

   (b) Three isomeric alkenes A, B and C with molecular formula C_5H_{10} on hydrogenation produce 2-methylbutane. A and B give the same tertiary alcohol on oxymercuration-demercuration. B and C give different primary alcohols on hydroboration-oxidation. Logically deduce structures of A, B and C. 3

   (c) Carry out the following conversions: 2+2

   (i) 2-butyne to (*Z*)-2,3-dideutero-2-butene

   (ii) 4, 4-dimethyl-2-pentene to 4, 4-dimethyl-1-pentene.

2. (a) Singlet carbene adds to *cis*-2-butene in a stereospecific manner whereas triplet carbene does not — Explain. 3

   (b) Identify the product(s) formed when 1-octene is reacted with NBS/CCl_4. Predict the relative yields with proper justification. 2

   (c) What happens when 1, 3-butadiene is treated with HBr at -80^{o} C and at 40^{o} C separately? Predict the product composition in each case and offer proper explanation in support of your answer. 3

   (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 on reductive ozonolysis. 1

UNIT-II

3. (a) Pivaloyl chloride (Me_3CCOCl) reacts with benzene in presence of anhydrous $AlCl_3$ to give mainly tert-butylbenzene whereas anisole under same reaction condition gives mainly *p*-methoxypivalophenone — Explain. 2

(b) Predict the favoured position of aromatic electrophilic substitution of the following compounds and justify your answer in each case: 2

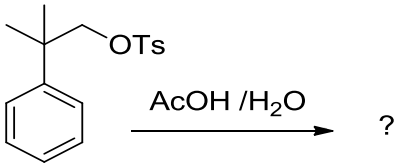
(i) $Ph–CH=CH–CO_2H$ (ii) $Ph–CO_2H$

(c) Compare reactivity of $PhNHCOCH_3$, aniline and benzene toward bromination reaction with proper justification. What is the major monosubstituted product formed during bromination of $PhNHCOCH_3$? 2

4. (a) Compare the reactivity of the following compounds towards nitration reaction using a mixture of concentrated HNO_3 and H_2SO_4: 2

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

(b) Predict the product giving proper mechanism. 2



(c) Account for the following observation: 2

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

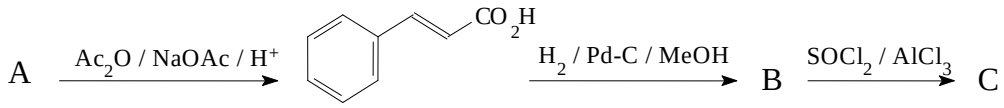
UNIT-III

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. 4

(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

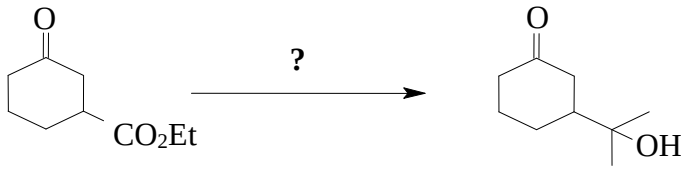
(c) Write down all the possible products from a mixed Claisen condensation with $CH_3CH_2CH_2COOCH_3$ and $PhCH_2COOCH_3$. 2

(d) In the following reaction sequence, identify A, B and C. Suggest suitable mechanism for the conversion from B to C. 3



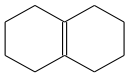
(e) α, β-unsaturated acid, $RCH_2CH=CHCO_2H$ decarboxylates readily on heating but $R_3CCH=CHCO_2H$ does not. — Why? 2

(f) Carry out the following conversion applying protection / deprotection technique. 2

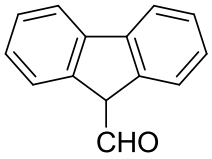


(g) Optically active PhCOCH(Et)Me is racemised on base treatment but $PhCOCH_2CH(Et)Me$ does not — Explain. 3

6. (a) Identify the products the following reaction. 3+3+2

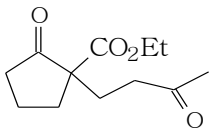
(i)  $\xrightarrow{O_3 / Zn\text{-}AcOH}$ **A** $\xrightarrow{NaOEt / EtOH}$ **B** $\xrightarrow[\text{Ethylene glycol / Heat}]{H_2N\text{-}NH_2 / KOH}$ **C**

(ii)

(iii)  + $H\overset{*}{C}HO$ $\xrightarrow{OH^- / H_2O}$ G + H

$\overset{*}{C} \equiv C^{14}$

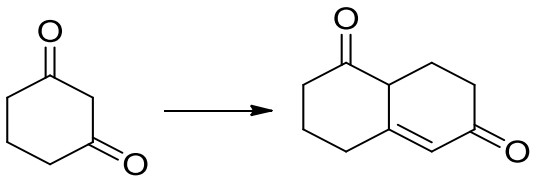
(b) When the following compound is treated with NaOEt/EtOH, two isomeric compounds (A) and (B) are obtained. Give suitable mechanism for the formation of the products. 3

 $\xrightarrow{NaOEt / H^+}$ A + B

(c) Synthesis of 2,2,5,5-Tetramethylhex-3-ene cannot be accomplished by Witting reaction — Explain. 2

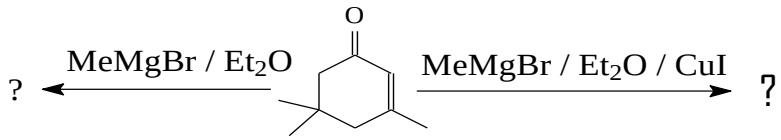
(d) Semicarbazide hydrochloride alone does not react with a ketone to give semicarbazone but when mixed with sodium acetate — it does — Why? Which nitrogen is involved in the reaction and why? 3

(e) Convert: 2



UNIT-IV

7. (a) Give the products with proper explanations: 2



(b) Carry out the following conversion involving organometallic reagents: 2

$(Me_2CH)_2CO \longrightarrow (Me_2CH)_3COH$

(c) Why Zn is a specific reagent for Reformatsky reaction? 2

8. (a) Convert the following using organometallic reagents: 2

$Me_2CO \longrightarrow Me_2C(OH)CH_2COOH$

(b) What happens when $PhCH_2MgBr$ is treated with HCHO followed by acidification? 2

(c) How can you prepare the acid $R_3C–CO_2H$ from R_3COH? 2

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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