



WEST BENGAL STATE UNIVERSITY

B.Sc. Honours 4th Semester Examination, 2020

CEMACOR10T-CHEMISTRY (CC10)

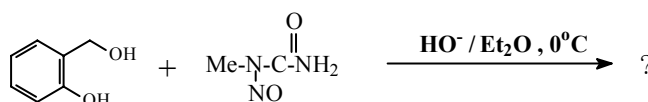
Time Allotted: 2 Hours

Full Marks: 40

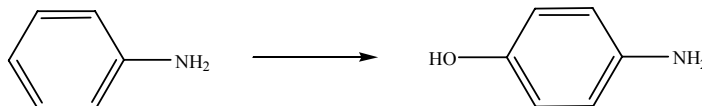
*The figures in the margin indicate full marks.
Candidates should answer in their own words and adhere to the word limit as practicable.
All symbols are of usual significance.*

Answer any **four** questions taking **one** from each unitUnit-I

1. (a) Nitriles undergo both acidic and alkaline hydrolysis but isonitriles are hydrolysed only by acids. Explain with mechanism. 2
- (b) Give the product with plausible mechanism explanation of the following reaction. 2



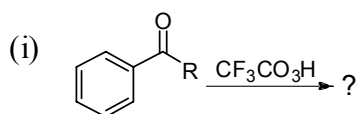
- (c) Carry out the following conversions. 2



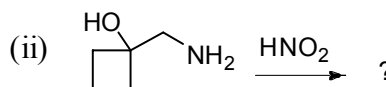
2. (a) Compare the reactions of aniline, N-methyl aniline and N,N-dimethylaniline towards benzenesulfonyl chloride and aq. KOH. How can you utilize this reaction for the separation of primary, secondary and tertiary amines? 2
- (b) How can you chemically distinguish between 4-nitro toluene and PhCH_2NO_2 ? 2
- (c) How can you convert aniline into 1, 2, 3-tribromobenzene? 2

Unit-II

3. (a) Identify the products in the following and show the plausible mechanism involved. 2+2



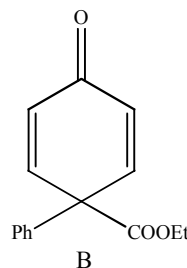
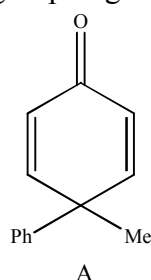
Case I: $\text{R} = \text{tBu}$
Case II: $\text{R} = \text{Me}$



(b) Explain the following observations.

2+2

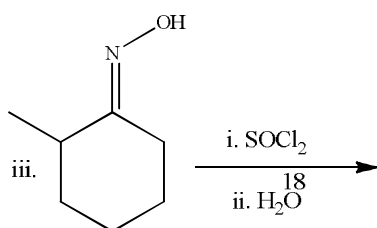
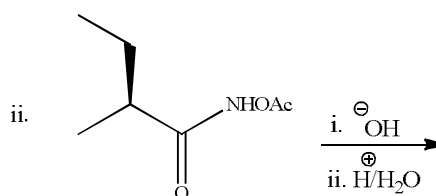
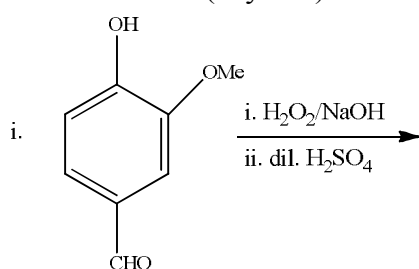
- (i) In the dienone-phenol rearrangement of compound A the phenyl group migrates but in the dienone-phenol rearrangement of compound B the $-\text{COOEt}$ group migrates.



- (ii) In the Hofmann degradation of RCONH_2 a small amount of CO(NHR)_2 and RNHCONHCOR are produced along with R-NH_2 .

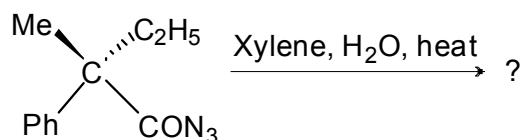
4. (a) Predict the products in the following reactions and formulate plausible mechanism for their formation. (any *two*).

2+2



- (b) Predict the product (with proper stereochemistry) in the following reaction with suitable mechanistic explanation.

2



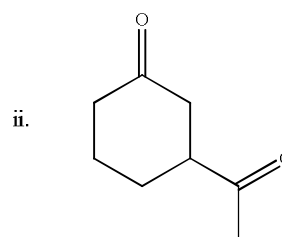
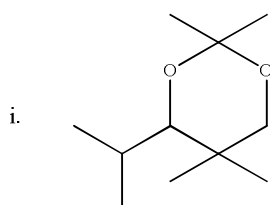
- (c) Two isomeric α -halo ketones **A** and **B** on treatment with NaOMe (separately) gave the same product $\text{PhCH}_2\text{CH}_2\text{CO}_2\text{Me}$. Identify **A** and **B**.

2

Unit-III

5. (a) Analyse the following molecules retro synthetically and suggest plausible synthetic route to them.

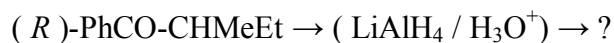
2½+2½



- (b) Give synthetic equivalent for the following species. 2



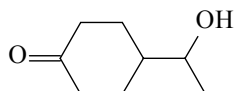
- (c) Predict the major product of the following reaction with proper stereochemistry. 2



- (d) Which combination of reagents is appropriate for the following transformation? 1



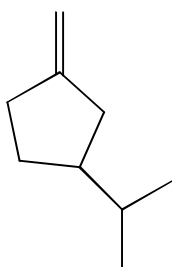
6. (a) Synthesize the following compound using Diels-Alder reaction one of the key step. 2



- (b) Explain with proper example: Illogical Nucleophile, Functional Group Addition. 3

- (c) Show disconnection of hexane-2,4-dione in terms of consonant and dissonant polarities. 2

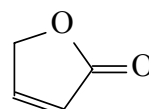
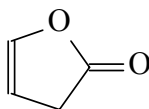
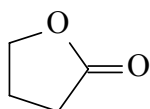
- (d) Outline a synthesis of the following molecule showing logical retro synthetic analysis. 3



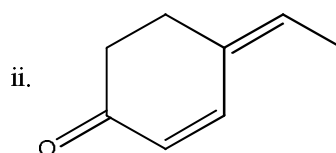
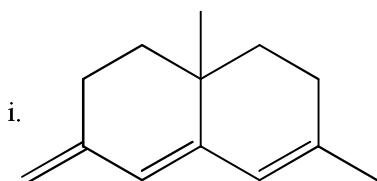
Unit-IV

7. (a) Concentrated solutions of $\text{C}_2\text{H}_5\text{OH}$ and $\text{HOCH}_2\text{CH}_2\text{OH}$ have broad O-H bands near 3350 cm^{-1} . On dilution with CCl_4 , the spectrum of ethylene glycol does not change but that of the alcohol shows a sharp peak at 3600 cm^{-1} replacing the band at 3350 cm^{-1} . Provide a suitable explanation in support of this observation. 3

- (b) Arrange the following compounds in order of increasing carbonyl stretching frequencies with proper explanation. 2



- (c) Calculate λ_{max} values for the following compounds using Woodward Fieser rule. 2+2



- (d) Compound B ($C_3H_6Cl_2$) displays the following spectroscopic data. 4
- UV : $\lambda_{max}(\epsilon_{max})$: Transparent above 210 nm
- IR (cm^{-1}) : 2950, 1270, 690.
- 1H -NMR : δ (ppm) 1.25 (d, 3H, J 7 Hz), 3.6 (m, 1H), 3.2 (dd, 2H, J 7 Hz, 11 Hz).
- Deduce the structure of compound B and explain the spectroscopic data as far as practicable.
- (e) Toluene is oxidised to benzaldehyde. What changes would you expect in PMR spectral feature for the product with respect to that of the starting material? 2
- (f) Mention one solvent, other than $CDCl_3$, that acts as NMR-solvent. 1
8. (a) $PhCOCH_3$ gives two isomeric oximes. Both of them are separately treated with conc. H_2SO_4 to give the products **A** and **B** respectively. Identify the products on the basis of IR spectroscopy. 3
- (b) An organic compound of molecular formula, $C_9H_{10}O_2$ showed three peaks in the PMR spectrum as given below: δ 1.96, singlet, 3H; δ 5.0, singlet, 2H and δ 7.2, singlet, 5H. One of the intense IR bands of this compound appears at 1740 cm^{-1} . Deduce the structure of the compound and explain the spectral data. 3
- (c) Account for the following observations. 2+2+2
- (i) Although sp carbon is more electronegative than sp^2 carbon, alkenyl protons appear at higher δ value than alkynyl protons in 1H -NMR spectrum.
- (ii) Stretching of aldehydic C-H appears as a doublet and at higher wave number than alkenyl C-H.
- (iii) Homoannular dienes absorb at higher wavelength than heteroannular dienes.
- (d) 'C=C' stretching frequency of cyclobutene is at 1566 cm^{-1} but that of 1-methylcyclobutene is at 1641 cm^{-1} . Account for this observation. 2
- (e) What is bathochromic shift in UV spectroscopy? Explain with a suitable example. 2

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WEST BENGAL STATE UNIVERSITY
B.Sc. Honours 4th Semester Examination, 2021

CEMACOR10T-CHEMISTRY (CC10)

ORGANIC CHEMISTRY-IV

Time Allotted: 2 Hours

Full Marks: 40

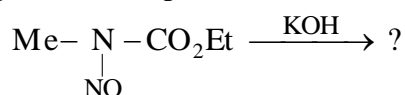
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Answer any four questions taking one from each unit

Unit-I

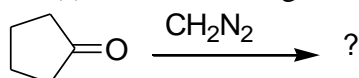
1. (a) Why ammonolysis on the corresponding alkyl bromides (RBr) cannot be used for the preparation of $t\text{BuNH}_2$ and $\text{Me}_3\text{CCH}_2\text{NH}_2$? How would you prepare these amines from carboxylic acids (RCO_2H)? 3

- (b) Give the product with plausible mechanism: 3

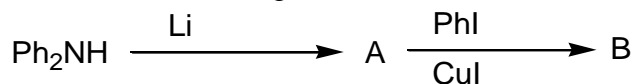


2. (a) Explain why benzene diazonium chloride couples with phenol in alkaline medium but not with anisole under the same reaction conditions. 2

- (b) Give the product(s) of the following reaction with plausible mechanism: 2



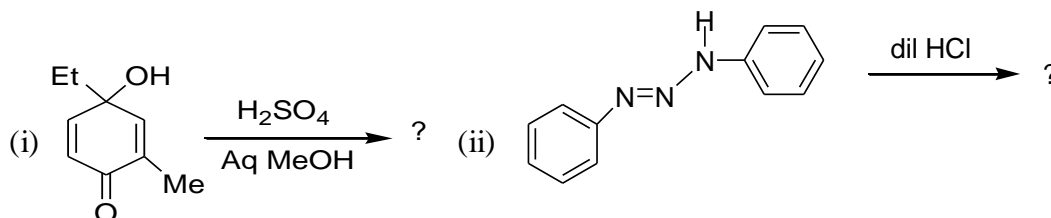
- (c) Identify A and B in the following: 2



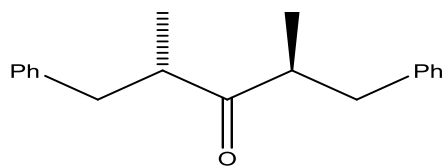
Unit-II

3. (a) In the Arndt-Eistert synthesis two equivalent of diazomethane is recommended. — Explain. 2

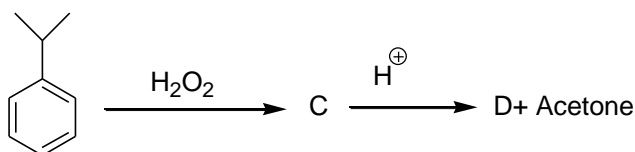
- (b) Identify the product(s) in the following with plausible mechanism. 2+2



- (c) Derive the product(s) of Baeyer-Villiger rearrangement on the following enantiomerically pure ketone. Suggest mechanism and comment on the stereochemistry of the product(s).

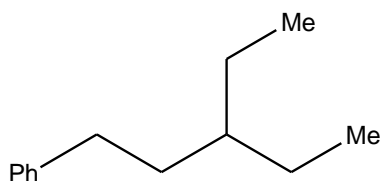


4. (a) Carry out the following conversion and suggest plausible mechanism (any *two*). 2+2
- Acetophenone to 2-phenylpropanal
 - Phenol to catechol
 - p*-Hydroxyacetophenone to paracetamol.
- (b) The isomeric pinacols $\text{Ph}_2\text{C}(\text{OH})\text{C}(\text{OH})\text{Me}_2$ and $\text{PhMeC}(\text{OH})\text{C}(\text{OH})\text{PhMe}$ undergo acid-catalyzed rearrangement to afford a common product. — Explain. 2
- (c) Identify C and D with proper mechanistic explanation. 2

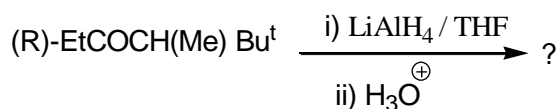


Unit-III

5. (a) Draw the scheme for retro-synthetic analysis of the following hydrocarbon using FGA strategy. Also, depict the synthetic pathway of it. 3

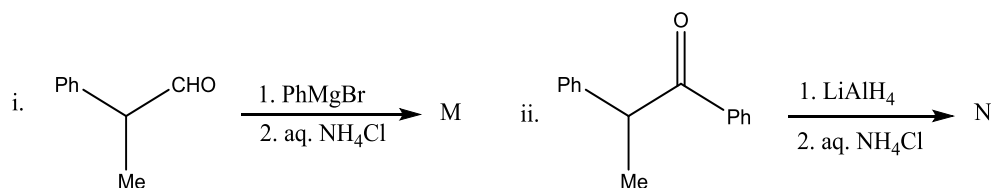


- (b) Predict the major product of the following reaction with reason. 3



- (c) Explain with suitable examples: Synthons and illogical electrophile. 2+2

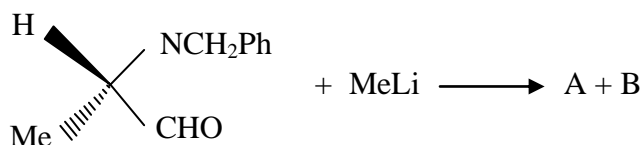
6. (a) Draw the structure of the major products (M and N) in the following reactions. Establish the stereoisomeric relationship between M and N and rationalize the results. 4



- (b) What do you mean by high dilution technique for the synthesis of large ring compounds? — Explain. 2
- (c) What do you mean by chemo-selective reaction? Give an example. 2

(d) Write the products with proper stereochemistry. Justify your answer.

2



Unit-IV

7. (a) Distinguish the following pair of compounds on the basis of their IR spectra: (any **two**) 2+2

- (i) Acetone and hexamethyl acetone
- (ii) Salicylic acid and *p*-hydroxy benzoic acid
- (iii) Phenyl acetate and methyl benzoate.

(b) The UV spectrum of mesityl oxide shows absorption bands at 321 and 230 nm in hexane. Assign them in terms of electronic transition. Depict the changes of this spectrum if the experiment is carried out in 95% ethanol solvent. Justify your answer. 3

(c) An organic compound of molecular formula $\text{C}_6\text{H}_{12}\text{O}$ shows a peak at 1715 cm^{-1} in its IR spectrum. The ^1H NMR spectrum of the compound displays two singlets at δ 0.9 and 2.2 in the ratio of 3:1. Deduce the structure of the compound and explain the spectral data. 3

(d) "Two protons are chemically equivalent but magnetically non-equivalent". Justify the statement with an example. 2

(e) Predict the number(s) of ^1H -NMR peak of chlorocyclopropane and justify. 2

(f) Esters of *o*-chlorobenzoic acid show two $\text{C}=\text{O}$ stretching frequencies. — Explain. 2

8. (a) Distinguish the following pairs by UV spectroscopy (any **two**): 3

- (i) *p*-cresol and anisole
- (ii) mesityl oxide and $\text{CH}_2 = \text{C}(\text{Me})\text{CH}_2\text{COMe}$
- (iii) aniline and cyclohexylamine.

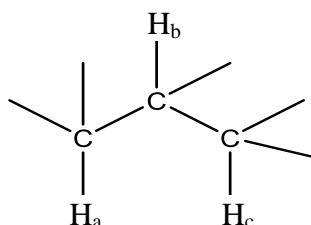
(b) Predict the organic compound of molecular formula $\text{C}_9\text{H}_{10}\text{O}_2$ from the following spectral data. 3

IR: 1740 cm^{-1} ; ^1H NMR: δ 1.96 (3H, s), 5.00 (2H, s) and 7.20 (5H, m).

(c) The stretching absorption maxima for C–H and C–D are approximately 2900 cm^{-1} and 2200 cm^{-1} respectively. Explain why. 2

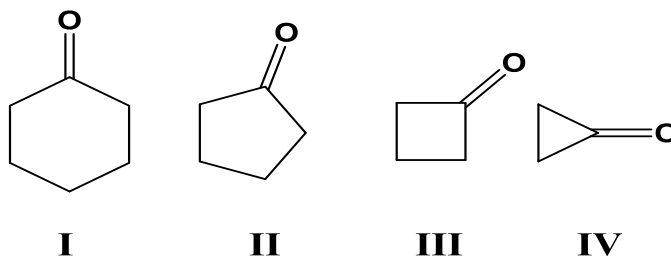
(d) Draw the splitting pattern for H_b in the ^1H -NMR spectrum of the fragment given below, where 2

- (i) $J_{ba} = 12\text{ Hz}$ and $J_{bc} = 6\text{ Hz}$ (ii) $J_{ba} = 12\text{ Hz}$ and $J_{bc} = 12\text{ Hz}$.



(e) Define the terms (i) up-field (ii) downfield shifts as used in NMR spectroscopy. 2

- (f) The UV absorption maxima of aniline in aqueous solution are different from those of benzene, but the positions of UV absorption maxima of aniline in acidic solution ($\text{pH} \approx 1$) are almost identical with benzene. — Explain. 2
- (g) Arrange the following compounds according to their increasing order of 'C=O' stretching frequency and give reason. 2



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WEST BENGAL STATE UNIVERSITY
B.Sc. Honours 4th Semester Supplementary Examination, 2021

CEMACOR10T-CHEMISTRY (CC10)

ORGANIC CHEMISTRY

Time Allotted: 2 Hours

Full Marks: 40

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Candidates should answer in their own words and adhere to the word limit as practicable.
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Answer any four questions taking one from each unit

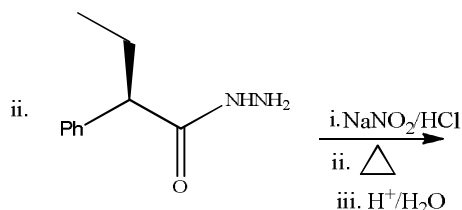
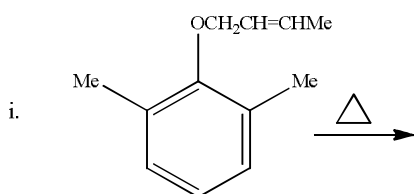
UNIT-I

1. (a) What is Mannich base? 2
 (b) Convert aniline to benzene. 2
 (c) State the action of $\text{NaNO}_2 / \text{HCl}$ on: 1+1
 (i) N-methylaniline (ii) N, N-dimethylaniline

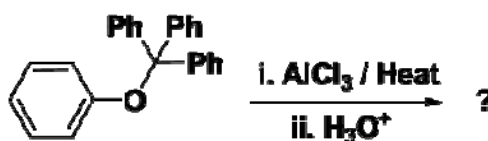
2. (a) How we can generate carbene from diazo methane? 2
 (b) Write short notes on NEF Carbonyl synthesis. 2
 (c) Convert: Phenol \longrightarrow *p*-aminophenol 2

UNIT-II

3. (a) "In the Arndt-Eistert synthesis two equivalent of diazomethane is used." — Explain the statement showing mechanism of the reaction. 2
 (b) Predict the products in the following reactions and formulate plausible mechanism for their formation. 2+2



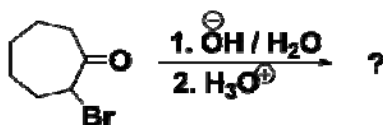
- (c) Explain the following rearrangement reaction in terms of thermodynamically and kinetically control product? 2



4. (a) In the dienone-phenol rearrangement of compound A the phenyl group migrates but in the dienone-phenol rearrangement of compound B the $-\text{COOEt}$ group migrates. Account for this observation. 3

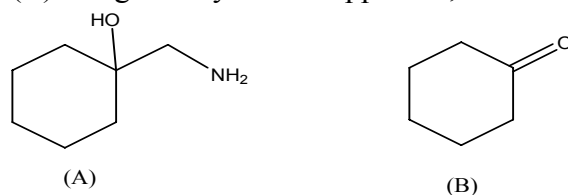


- (b) Show that Hofmann, Curtius, and Lossen reactions proceed through a common intermediate. Give proper evidence in favour of your answer. 3
- (c) Predict the product in the following reaction with plausible mechanistic explanation. 2

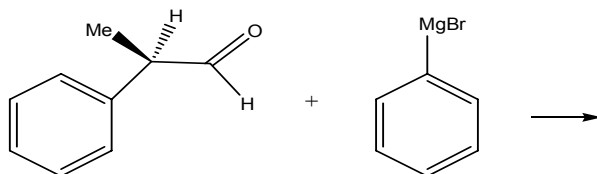


UNIT-III

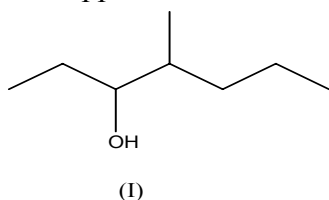
5. (a) Differentiate between stereoselective and stereospecific reaction with example. 2
- (b) What is meant by 'illogical electrophile' and 'illogical nucleophile'? Give examples. 2
- (c) Write down protection and deprotection method of Boc protected amine. 2
- (d) Synthesize (A) from (B) using retrosynthetic approach, 2



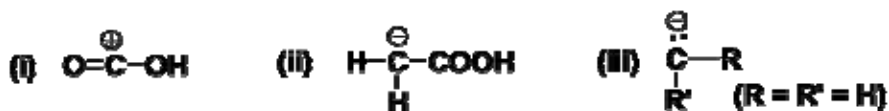
- (e) Predict the major and minor product. 2



6. (a) Differentiate between diastereoselectivity and enantioselectivity with example. 2
- (b) Define the terms disconnection and synthon. 2
- (c) Write down protection and deprotection method of CBz protected amine. 2
- (d) Synthesize (I) using retrosynthetic approach. 2



- (e) Write down the synthetic equivalents of any *two* of the following synthons. 2

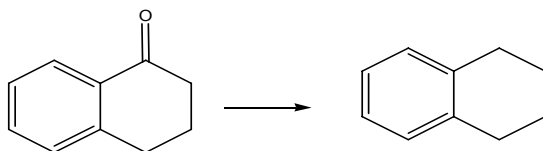


UNIT-IV

7. (a) How can you distinguish between anisole and *p*-cresol by UV spectroscopy? 2
 (b) Calculate λ_{\max} values for the following compounds using Woodward Fieser rule. 2+2



- (c) Why carbonyl stretching frequency in acetone is lower than that in acetyl chloride? 2
 (d) Write down different types of stretching and bending vibrations. 2+2
 (e) A compound $C_4H_6O_2$ shows a very strong IR band at 1720 cm^{-1} and only one singlet signal in its ^1H NMR spectrum. Analyze the compound. 3
 (f) Distinguish *o*-hydroxy benzaldehyde and *p*-hydroxy benzaldehyde by IR spectroscopy. 1
8. (a) A compound of molecular formula $C_6H_{12}O$ shows a very strong IR band at 1705 cm^{-1} and two singlet signals at δ 2.1 and 1.2 in its ^1H NMR spectrum. Analyze the compound. 3
 (b) Differentiate between *o*-dinitrobenzene and *p*-dinitrobenzene by ^1H NMR spectra. 2
 (c) How can you distinguish between cyclohexanone and cyclopentanone by IR spectroscopy? 2
 (d) The position of UV absorption maxima of aniline in aqueous solution are different from those of benzene but are almost identical with those of benzene in a solution of $\text{pH} = 1$. 2
 (e) Between *cis*-stilbene and *trans*-stilbene, which one will absorb at longer wavelength and why? 2
 (f) How do you monitor the completion of the below reaction by IR spectroscopy? 2



- (g) Draw ^1H NMR signals of $\text{CH}_3\text{CH}_2\text{OH}$ showing the relative chemical shifts, integration and spin-spin coupling pattern. 3

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WEST BENGAL STATE UNIVERSITY

B.Sc. Honours 4th Semester Examination, 2022

CEMACOR10T-CHEMISTRY (CC10)

ORGANIC CHEMISTRY-IV

Time Allotted: 2 Hours

Full Marks: 40

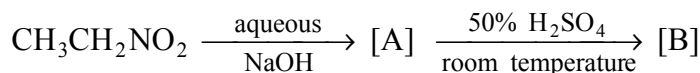
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1. (a) How would you chemically distinguish the following pair of compounds? 2

(i) Benzyl cyanide and benzyl isocyanide

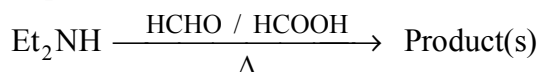
(ii) N-methylaniline and N, N-dimethylaniline.

- (b) Explain the products [A] and [B] with proper mechanism of the reaction. 2

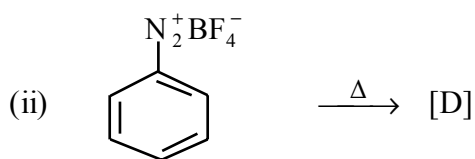
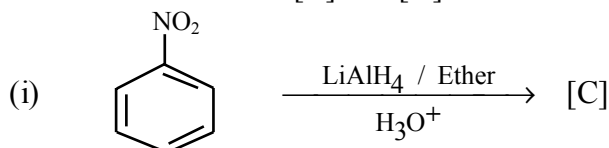


- (c) How can you prepare N-methylaniline from aniline? 2

2. (a) Suggest the product(s) and give the mechanism for the following reaction: 2



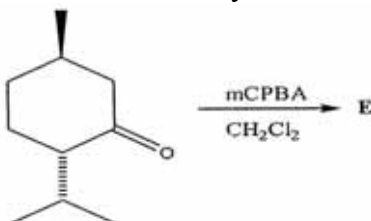
- (b) Give the structures of [C] and [D]: 2



- (c) How can you convert aniline to 1,3,5-tribromobenzene? 2

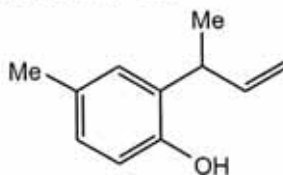
Unit-II

3. (a) Draw the structure of E with the proper configuration of the stereogenic centres and give plausible mechanistic steps. Discuss the effect of stereoelectronic factors for the determination of regio and stereoselectivity. 4



(b) Carry out the following conversions:

2+2

(i) Phthalic anhydride \longrightarrow anthranilic acid(ii) *p*-Cresol \longrightarrow 

4. (a) Outline two methods for the preparation of phenyl acetate. Rationalise the products in the reaction of phenyl acetate and anhydrous AlCl_3 (Friedel-Crafts conditions) with plausible mechanism. Explain the role of solvents and temperature in the control of product ratio.

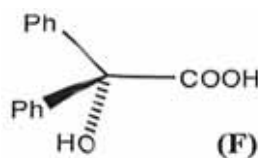
4

(b) Convert benzoyl chloride to phenylacetic acid in one-step. Suggest plausible mechanism with a comment on the intermediate.

2

(c) Convert benzoin to the α -hydroxyacid (**F**) in two steps and suggest plausible mechanism for step two only.

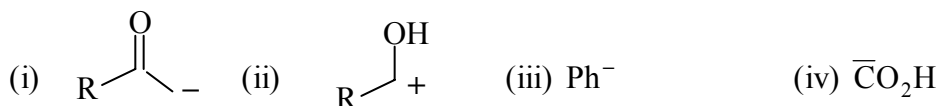
2



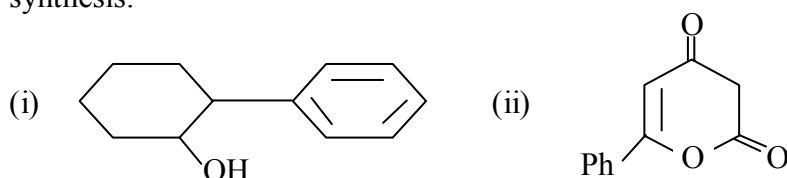
Unit-III

5. (a) Give the synthetic equivalent for the following species:

2

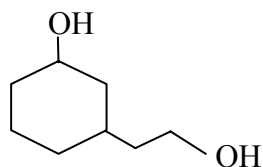


(b) Show the retrosynthetic analysis of the following compounds and then carry out the synthesis: $1\frac{1}{2} + 1\frac{1}{2}$



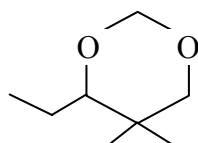
(c) Plan a retrosynthesis followed by the synthesis of the following by FGI approach.

3



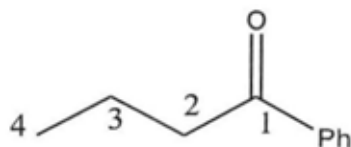
(d) Propose a synthesis of the following compound:

2

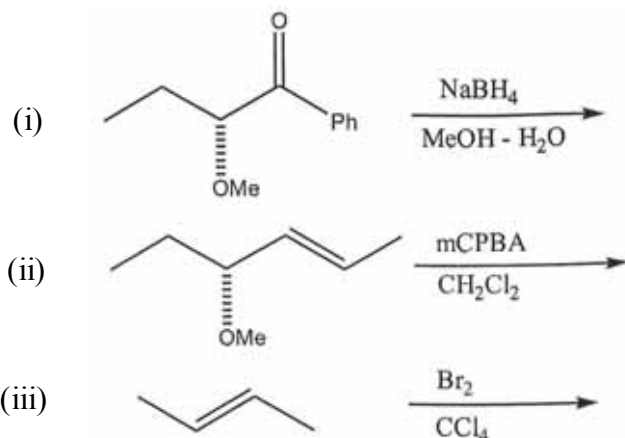


6. (a) Depict the disconnections, as indicated for the retrosynthesis of the following ketone and then draw the synthons and the corresponding synthetic equivalents. Also, classify all the synthons as logical / illogical and donor / acceptor terminology.

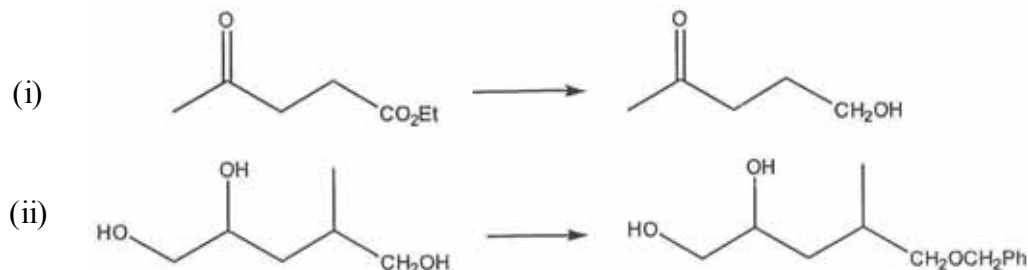
4



- (i) FGI followed by C – C disconnection
 (ii) 1,2 C – C disconnection
 (iii) 2,3 C – C disconnection
 (iv) 3,4 C – C disconnection.
- (b) Predict the product(s) in the reactions given below and comment whether these are stereoselective or stereospecific reactions. 3



- (c) Carry out the following conversions using protection / deprotection strategy. 3



Unit-IV

7. (a) Sketch and label the possible bending vibrational modes in CH_2Cl_2 . 2
 (b) What are the radiation sources of IR spectrometer and UV spectrometer? 2
 (c) What are the significance of the terms: (i) absorbance and (ii) vacuum UV? 2
 (d) Describe Fermi coupling. Which region in IR spectrum is known as fingerprint region? Describe its significance. 2
 (e) Distinguish the following pair of compounds using spectroscopy: 3
- (i) (IR spectroscopy)
 (ii) *cis* and *trans* stilbene (UV spectroscopy)
 (iii) $\text{CH}_3 - \text{CH}_2 - \text{C} \equiv \text{CH}$ and $\text{H}_3\text{C} - \text{C} \equiv \text{C} - \text{CH}_3$ (^1H NMR)
 (f) Aromatic protons are more deshielded than ethylenic protons, although both the types of protons are attached to sp^2 hybridised C-atom. — Explain. 2

- (g) An organic compound having molecular formula $C_8H_7NO_3$ shows a strong IR bond at 1690 cm^{-1} and three signals at
- δ 8.5 (doublet)
 δ 7.9 (doublet)
 δ 2.5 (singlet)
- in its ^1H NMR spectra. Establish the structure of the compound. 3
8. (a) In IR spectroscopy ethylacetoacetate shows the peaks at 1715 cm^{-1} , 1690 cm^{-1} , 2900 cm^{-1} and 3500 cm^{-1} . How will you explain it? 2
- (b) Define the following terms: 2
- (i) Hypochromic effect, (ii) Hypsochromic effect
- (c) How would you distinguish 4-nitro-N,N-dimethylaniline and acidified 4-nitro-N,N-dimethylaniline by UV spectroscopy? 2
- (d) Predict and label the chemical shifts in δ_{ppm} and the splitting pattern of the nonequivalent Hs of butanone. Express the difference of chemical shift value in Hz between the upfield and downfield Hs in butanone. 3
- (e) The compound (X) is obtained as major product after the mononitration of toluene. Compound X on reduction with Sn and concentrated HCl gives compound Y. Compare the ^1H -NMR spectra of X and Y. 2
- (f) What are the two probable products (enone) in the aldol condensation of acetone? How would you distinguish them by UV, IR and ^1H -NMR spectroscopy? 3
- (g) Why is tetramethylsilane (TMS) preferred as an internal standard in ^1H -NMR experiment? 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.

—x—