

CHEMISTRY

PAPER—III

Time Allowed : Three Hours

Maximum Marks : 200

QUESTION PAPER SPECIFIC INSTRUCTIONS

Please read each of the following instructions carefully before attempting questions

There are **TEN** questions divided under **TWO** Sections.

Candidate has to attempt **SIX** questions in all.

Question No. **1** in Section—A and Question No. **6** in Section—B are **compulsory**. Of the remaining questions, candidates have to answer **FOUR** questions, choosing **TWO** from each Section.

The number of marks carried by a question/part is indicated against it.

Neat sketches are to be drawn to illustrate answers, wherever required. These shall be drawn in the space provided for answering the question itself.

Unless otherwise mentioned, symbols and notations have their usual standard meanings.

Assume suitable data, if necessary, and indicate the same clearly.

Attempts of questions shall be counted in sequential order. Unless struck off, attempt of a question shall be counted even if attempted partly.

Any page or portion of the page left blank in the Question-cum-Answer (QCA) Booklet must be clearly struck off.

Answers must be written in **ENGLISH** only.

1. (a) A geologist received certain samples as follows :

Sample	Weight of sample (g)
Sample 1	2.50×10^{-1}
Sample 2	2.40×10^{-3}
Sample 3	5.00×10^{-5}
Sample 4	1.50×10^{-2}
Sample 5	7.00×10^{-5}
Sample 6	1.75×10^{-3}
Sample 7	0.75×10^{-1}

Classify the above samples as per their respective sample size following the sampling protocol for analytical chemist.

- (b) In gas chromatography, what is the effect of stationary-phase film thickness on gas chromatograms?
- (c) An amine sample is analyzed as the picrate derivative. A 0.05 g sample is reacted with picric acid and diluted to 1 L deionized water. The solution exhibits an absorbance of 0.40 in a 1 cm cell. What is the percentage of amine in the sample?
 $[\lambda_{\max} = 359 \text{ nm}; \quad \epsilon = 1.25 \times 10^4 \text{ cm}^{-1} \text{ mol}^{-1} \text{ L}; \quad \text{formula weight of the amine} = 310]$
- (d) What is the principle used in VG-AAS? Give the names of two elements that are measured with better detection limit using VG-AAS than by flame AAS.
- (e) Name three gases used for purging in thermogravimetric analysis (TGA). Justify your answer.
- (f) What is the cause of fluorescence in X-ray diffraction? How does fluorescence phenomenon impact X-ray diffraction data?
- (g) (i) What is the purpose of using argon gas in ICPMS?
 (ii) Why is HCl or HClO_4 not recommended for sample preparation for arsenic analysis by ICPMS?

- (h) A solution comprising 1.0 g pyrolusite is treated with 100 mL of 0.1 N oxalic acid and H_2SO_4 . The excess oxalic acid requires 27 mL of 0.05 N KMnO_4 for complete titration. Find the amount of MnO_2 (in wt%) in the sample. [Given : Molar mass of $\text{MnO}_2 = 87 \text{ g mol}^{-1}$]

5

2. (a) The first three peaks in an X-ray diffractogram (XRD) of metal M are obtained at 2θ values of 38.6° , 55.7° and 70.0° , using $\text{Cu K}\alpha$ radiation ($\lambda = 1.542 \text{ \AA}$). Compare the crystal structure and atomic radii with those given in the table below, and identify M :

Metal	Crystal structure	Atomic radius ($\text{\AA}$)
Al	FCC	1.431
Au	FCC	1.442
Pt	FCC	1.387
Cr	BCC	1.249
Mo	BCC	1.363
Ta	BCC	1.429
Ti	HCP	1.445
Zn	HCP	1.332
Cd	HCP	1.490

15

- (b) (i) Why is quantitative analysis of Fe^{2+} by spectrophotometric method drastically improved by complexation with 1,10-phenanthroline? What analytical parameters are improved?

3+4

- (ii) How will you validate the above method of analysis?

3

- (c) How can the age of a geological deposit be determined by ICPMS analysis?

5

3. (a) Aluminium (Al) content (in g) in a 100 g bauxite sample is determined by two different laboratory methods, as given below :

Sl. No.	Method-A	Method-B
1.	51.0	51.1
2.	51.9	52.0
3.	52.3	52.7
4.	54.4	54.6
5.	50.9	51.2
6.	53.1	53.4

Calculate the 'variance' of the analyses by both methods (A and B) above and compare their precision through F -test, and state which of the methods, A or B, is significant for analysis of Al in bauxite ore.

[F -table is provided in the next page]

10

F-table

Probability level	ϕ_2	ϕ_1 (corresponding to greater mean square)											
		1	2	3	4	5	6	7	8	9	10	15	∞
0.10	1	39.9	49.5	53.6	55.8	57.2	58.2	58.9	59.4	59.9	60.2	61.2	63.3
0.05		161.4	199.5	215.7	224.6	230.2	234.0	236.8	238.9	240.5	241.9	246.0	254.3
0.01		4052	4999	5403	5625	5764	5859	5928	5981	6023	6056	6157	6366
0.10	2	8.53	9.00	9.16	9.24	9.29	9.33	9.35	9.37	9.38	9.39	9.42	9.49
0.05		18.5	19.0	19.2	19.2	19.3	19.3	19.4	19.4	19.4	19.4	19.4	19.5
0.01		98.5	99.0	99.2	99.2	99.3	99.3	99.4	99.4	99.4	99.4	99.4	99.5
0.10	3	5.54	5.46	5.39	5.34	5.31	5.28	5.27	5.25	5.24	5.23	5.20	5.13
0.05		10.1	9.55	9.28	9.12	9.01	8.94	8.89	8.85	8.81	8.79	8.70	8.53
0.01		34.1	30.8	29.5	28.7	28.2	27.9	27.7	27.5	27.3	27.2	26.9	26.1
0.10	4	4.54	4.32	4.19	4.11	4.05	4.01	3.98	3.95	3.94	3.92	3.87	3.76
0.05		7.71	6.94	6.59	6.39	6.26	6.16	6.09	6.04	6.00	5.96	5.86	5.62
0.01		21.2	18.0	16.7	16.0	15.5	15.2	15.0	14.8	14.7	14.5	14.2	13.5
0.10	5	4.06	3.78	3.62	3.52	3.45	3.40	3.37	3.34	3.32	3.30	3.24	3.10
0.05		6.61	5.79	5.41	5.19	5.05	4.95	4.88	4.82	4.77	4.74	4.62	4.36
0.01		16.3	13.3	12.1	11.4	11.0	10.7	10.5	10.3	10.2	10.1	9.72	9.02
0.10	6	3.78	3.46	3.29	3.18	3.11	3.05	3.01	2.98	2.96	2.94	2.87	2.72
0.05		5.99	5.14	4.76	4.53	4.39	4.28	4.21	4.15	4.10	4.06	3.94	3.67
0.01		13.7	10.9	9.78	9.15	8.75	8.47	8.26	8.10	7.98	7.87	7.56	6.88
0.10	7	3.59	3.26	3.07	2.96	2.88	2.83	2.78	2.75	2.72	2.70	2.63	2.47
0.05		5.59	4.74	4.35	4.12	3.97	3.87	3.79	3.73	3.68	3.64	3.51	3.23
0.01		12.2	9.55	8.45	7.85	7.46	7.19	6.99	6.84	6.72	6.62	6.31	5.65
0.10	8	3.46	3.11	2.92	2.81	2.73	2.67	2.62	2.59	2.56	2.54	2.46	2.29
0.05		5.32	4.46	4.07	3.84	3.69	3.58	3.50	3.44	3.39	3.35	3.22	2.93
0.01		11.3	8.65	7.59	7.01	6.63	6.37	6.18	6.03	5.91	5.81	5.52	4.86
0.10	9	3.36	3.01	2.81	2.69	2.61	2.55	2.51	2.47	2.44	2.42	2.34	2.16
0.05		5.12	4.26	3.86	3.63	3.48	3.37	3.29	3.23	3.18	3.14	3.01	2.71
0.01		10.6	8.02	6.99	6.42	6.06	5.80	5.61	5.47	5.35	5.26	4.96	4.31
0.10	10	3.29	2.92	2.73	2.61	2.52	2.46	2.41	2.38	2.35	2.32	2.24	2.06
0.05		4.96	4.10	3.71	3.48	3.33	3.22	3.14	3.07	3.02	2.98	2.85	2.54
0.01		10.0	7.56	6.55	5.99	5.64	5.39	5.20	5.06	4.94	4.85	4.56	3.91
0.10	12	3.18	2.81	2.61	2.48	2.39	2.33	2.28	2.24	2.21	2.19	2.10	1.90
0.05		4.75	3.89	3.49	3.26	3.11	3.00	2.91	2.85	2.80	2.75	2.62	2.30
0.01		9.33	6.93	5.95	5.41	5.06	4.82	4.64	4.50	4.39	4.30	4.01	3.36
0.10	15	3.07	2.70	2.49	2.36	2.27	2.21	2.16	2.12	2.09	2.06	1.97	1.76
0.05		4.54	3.68	3.29	3.06	2.90	2.79	2.71	2.64	2.59	2.54	2.40	2.07
0.01		8.68	6.36	5.42	4.89	4.56	4.32	4.14	4.00	3.89	3.80	3.52	2.87
0.10	16	3.05	2.67	2.46	2.33	2.24	2.18	2.13	2.09	2.06	2.03	1.94	1.72
0.05		4.49	3.63	3.24	3.01	2.85	2.74	2.66	2.59	2.54	2.49	2.35	2.01
0.01		8.53	6.23	5.29	4.77	4.44	4.20	4.03	3.89	3.78	3.69	3.41	2.75
0.10	24	2.93	2.54	2.33	2.19	2.10	2.04	1.98	1.94	1.91	1.88	1.78	1.53
0.05		4.26	3.40	3.01	2.78	2.62	2.51	2.42	2.36	2.30	2.25	2.11	1.73
0.01		7.82	5.61	4.72	4.22	3.90	3.67	3.50	3.36	3.26	3.17	2.89	2.21
0.10	60	2.79	2.39	2.18	2.04	1.95	1.87	1.82	1.77	1.74	1.71	1.60	1.29
0.05		4.00	3.15	2.76	2.53	2.37	2.25	2.17	2.10	2.04	1.99	1.84	1.39
0.01		7.08	4.98	4.13	3.65	3.34	3.12	2.95	2.82	2.72	2.63	2.35	1.60
0.10	∞	2.71	2.30	2.08	1.94	1.85	1.77	1.72	1.67	1.63	1.60	1.49	1.00
0.05		3.84	3.00	2.60	2.37	2.21	2.10	2.01	1.94	1.88	1.83	1.67	1.00
0.01		6.63	4.61	3.78	3.32	3.02	2.80	2.64	2.51	2.41	2.32	2.04	1.00

(b) The following data is given for Fe analysis by atomic absorption spectrometry :

Concentration of Fe (mg/L)	Instrument response (absorbance)
0.000	0.040
2.000	0.150
5.000	0.380
15.000	1.020
Unknown	0.832

The least square fit of the calibration data is given as $y = 0.064x + 0.032$.

(i) Can we estimate Fe in a sample with concentration 0.200 mg/L? Explain.

(ii) Determine the concentration of Fe in the unknown sample.

[Given : The blank sample was measured for 25 times and the standard deviation of the mean value (i.e., 0.040) is 0.008]

6+4

(c) A sample of petroleum distillate during Doctor Test is shaken with a faint yellow colour solution **X**. No change in colour is observed. Then some sulphur is added and the solution turns dark brown. This happens when **Y** species is present in a petroleum distillate. What are **X** and **Y**?

2+3

(d) Calculate the resolution of two analytes, whose chromatographic peaks are separated by 4 min with bandwidth of each analyte as 0.5 min.

5

4. (a) Describe how the ion-exchange capacity of an anion-exchange resin can be measured using standard NaOH, standard HCl or any other reagent.

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(b) In the thermogravimetric analysis (TGA) of 0.45 g of Ca(OH)_2 sample, the losses in weight at different temperatures are as follows :

(i) 0.025 g at 100 °C–150 °C

(ii) 0.040 g at 500 °C–560 °C

(iii) 0.023 g at 900 °C–950 °C

What is the composition of calcium hydroxide in the sample?

10

- (c) Using the following data, find the difference between gross calorific value and net calorific value of a coal sample whose composition (by weight) is carbon = 85.0%, hydrogen = 10.29% and ash = 4.71%.

Data :

Mass of the coal sample fired in a bomb calorimeter = 1.5 g

Mass of water taken in the calorimeter = 2500 g

Mass equivalent of the calorimeter = 2750 g

Rise in temperature in the calorimeter = 3.0 °C

Specific heat of water = 1 cal/(g °C)

Latent heat of condensation of steam = 540 cal/g

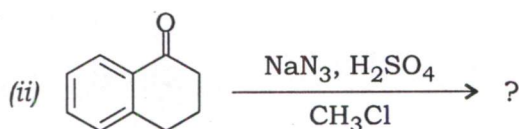
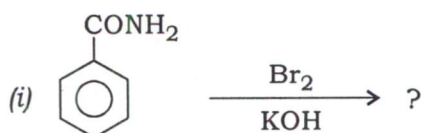
Assume all correction factors to be negligible.

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5. (a) Interference filters are used as wavelength selectors. Sketch a typical interference filter and explain how interference filters provide narrow band of radiation. 10
- (b) An organic acid dissolved in 50 mL of water is equilibrated with 50 mL of ether. The distribution coefficient (K_D) is 50 and the dissociation constant (K_a) is 5.0×10^{-5} . Calculate the distribution ratio (D), if the aqueous layer is at pH 3, pH 5 and pH 7. 10
- (c) How will Cu content in a brass sample be quantitatively analyzed volumetrically without interference from Zn present? Describe the method and steps involved in the analysis. 10

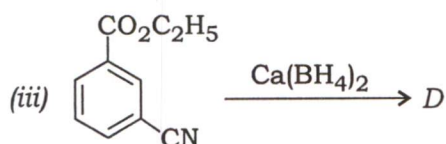
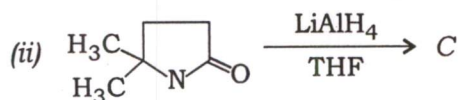
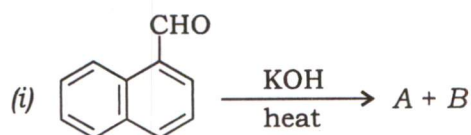
SECTION—B

6. (a) Predict the major product in the following reactions, and name the reactions :



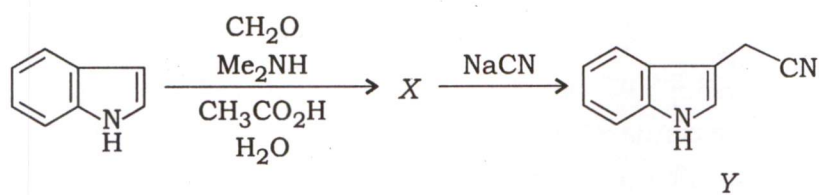
2+2

(b) Identify the major products in the given reactions :



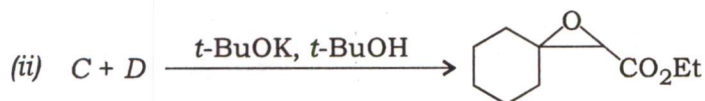
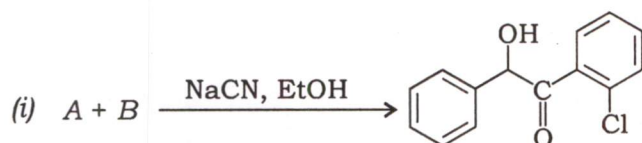
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(c) Identify the major product (X) formed in the following reaction sequence and suggest a suitable mechanism for the conversion of X → Y :



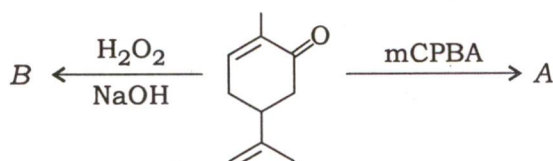
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(d) Predict the reactants and identify the name of the reactions in the following :



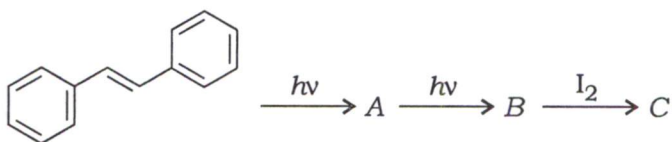
2+2

(e) Identify the major products A and B formed in the following reactions :



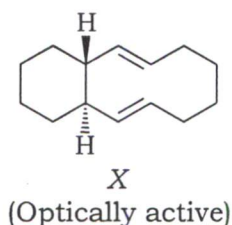
2+2

- (f) Predict the major products (A–C) formed (with appropriate stereochemistry, if any) in the following reaction sequence :



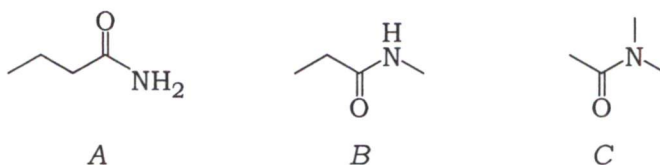
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- (g) The optically active compound (X) racemizes on heating. Explain the observation :



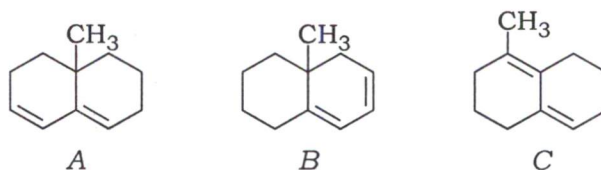
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- (h) In IR spectrum, the selected bands observed for the unknown amide having molecular formula C_4H_9NO are 3350, 3200, 2925, 1660 and 1420 cm^{-1} . Among the following, identify the amide that gives the observed bands and justify your answer :



4

- (i) Using Woodward-Fieser rule, calculate λ_{max} for the following compounds and arrange them in the order of increasing λ_{max} :

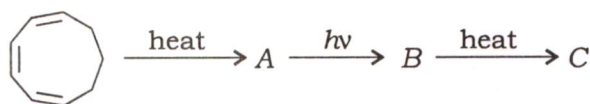


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- (j) The unknown dihaloalkane gives a molecular ion peak at $m/z = 128$ with a relative intensity of 75. The relative intensities of $M+2$ and $M+4$ peaks are 100 and 25 respectively. Identify the halides present in the compound and justify your answer.

4

7. (a) Predict the major products (A-C) formed (with appropriate stereochemistry, if any) in the following reaction sequence. Describe the mode of cyclization involved under thermal and photochemical conditions :



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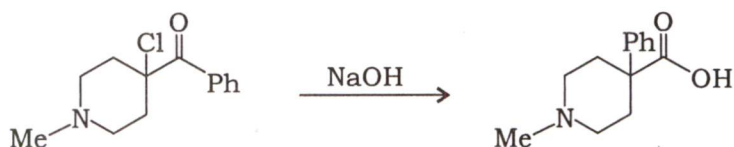
- (b) (i) $^1\text{H-NMR}$ spectrum of bullvalene (X) shows a single signal at $\delta 4.22$ ppm at 10°C . Explain the observation :



Bullvalene (X)

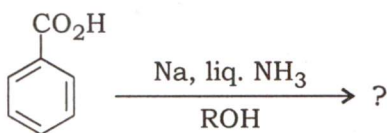
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- (ii) Suggest a suitable reaction mechanism for the following reaction :



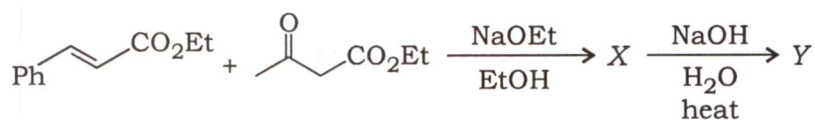
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- (c) (i) Identify the product and provide the name and mechanism for the following reaction :



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- (ii) Predict the major products X and Y formed in the following reaction sequence. Suggest a suitable mechanism for the formation of X :



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8. (a) In a solution, acetylacetone exhibits keto-enol tautomerism. The chemical shift (δ in ppm) and their intensity observed in the $^1\text{H-NMR}$ of acetylacetone in CDCl_3 is given below.

[O—H signal of the enol tautomer is not shown]

δ (in ppm)	Intensity
5.52	360
3.61	90
2.24	270
2.04	2160

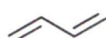
- (i) Assign the signals to the corresponding hydrogen in the tautomers.
- (ii) Calculate the ratio of keto-enol tautomers and identify the major tautomer present in the solution.

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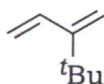
- (b) (i) Draw the π -molecular orbitals of 1,3-butadiene and arrange them in the order of their energy. Assign the HOMO and LUMO under thermal and photochemical conditions.

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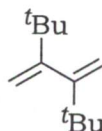
- (ii) Arrange the following dienes in the increasing order of reactivity towards maleic anhydride. Explain your answer :



A



B



C

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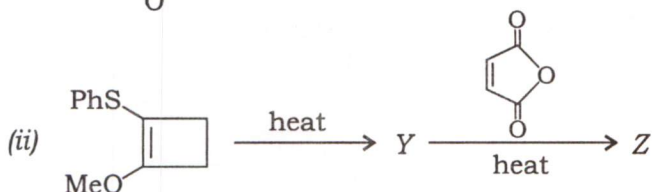
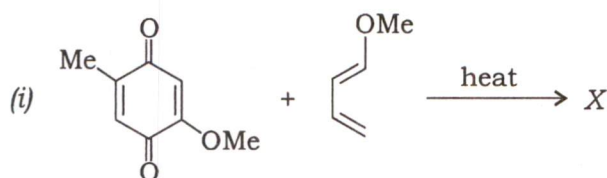
- (c) (i) The major product formed on ethyl propionate with KOH in ethanol gives a strong $\text{C}=\text{O}$ stretching frequency at 1745 cm^{-1} and 1725 cm^{-1} in IR spectrum. Identify the major product and suggest the suitable mechanism.

5

- (ii) The unknown monoterpene on complete reductive ozonolysis with O_3 and Me_2S gave equimolar mixture of formaldehyde, acetone, pyruvaldehyde and malondialdehyde. Draw the structure of all the products and deduce the structure of the monoterpene.

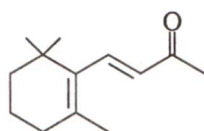
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9. (a) Draw the major products formed in the following reactions and describe the process involved :

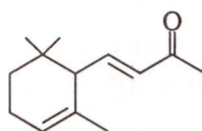


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- (b) (i) Among the following, identify the ionone that will give the peak at $m/z = 136$ in EI mass spectrum and explain your answer :



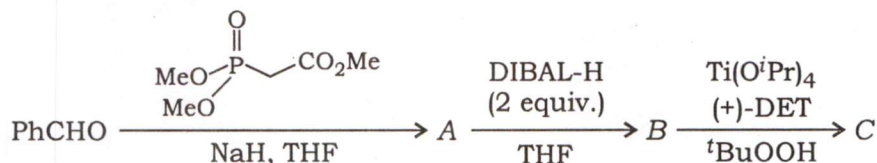
α -ionone



β -ionone

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- (ii) Draw the major products (A–C) formed (with appropriate stereochemistry, if any) in the following reaction sequence :



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- (c) Propose the mechanism for polymerization of alkene C_2H_4 when treated with Ziegler-Natta catalyst. Predict the nature of conductivity of the formed polymer and justify your answer.

10

10. (a) An organic compound having molecular formula $C_{10}H_{16}O_4$ gave the following spectral data :

IR : Significant absorption bands at 2904, 1725, 1641, 1244 cm^{-1}

1H -NMR (400 MHz, $CDCl_3$) : δ 4.23 (q, $J = 7.2$ Hz, 4 H), 2.06 (s, 6 H)

and 1.29 (t, $J = 7.2$ Hz, 6 H)

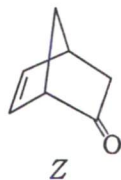
^{13}C -NMR (100 MHz, $CDCl_3$) : δ 165.7, 154.9, 124.8, 60.8, 23.1 and 14.1

EI-MS : Prominent peaks at m/z 99 and 155

Deduce the structure of the compound and explain the data.

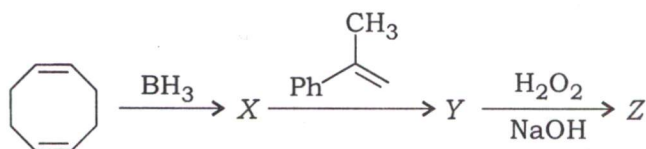
10

- (b) (i) Suggest a suitable method for the synthesis of the following compound (Z) from cyclopentadiene :



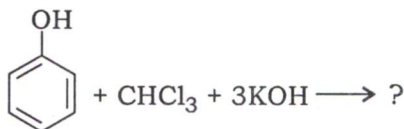
5

- (ii) Identify the major products (X-Z) formed in the following reaction sequence :



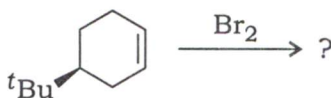
5

- (c) (i) Predict the major product in the given reaction with possible mechanism. Also mention the fast and slow steps in the mechanism :



5

- (ii) Identify the major product formed in the following reaction and explain the stereochemical outcome :



5
