WEST BENGAL STATE UNIVERSITY

B.Sc. Honours PART-II Examinations, 2018

CHEMISTRY-HONOURS

PAPER-CEMA-IV

Time Allotted: 2 Hours | Full Marks: 50

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.

CEMAT-24-PA

Answer any *two* questions taking *one* from each unit

Unit-I

1. (a) $\psi = \psi_1 + \sqrt{3}\psi_2$, where ψ_1 and ψ_2 are normalized and mutually orthogonal functions. Normalize ψ. 3

   (b) The stopping potential for photo electrons emitted from a surface irradiated with light of wavelength 3000 Å is 1.91 V. When the incident wavelength is changed the potential is found to be 0.9 V. What is the new wavelength? 4

   (c) If $\hat{A} = \frac{d^2}{dx^2}$ and $\hat{B} = x$. Find out whether (i) $\hat{A}$, $\hat{B}$ commute (ii) $(e^x + \sin x)$ is an eigen function of $(\hat{A} + \hat{B})$. 4

   (d) Show that adding a constant 'c' to the potential energy leaves the stationary state wave functions unchanged and simply adds 'c' to the energy eigenvalues. 2

2. (a) Justify or criticize the following statements: 2+2

   (i) The state function ψ must be a real function.

   (ii) The term *state* and *energy level* are synonymous in quantum mechanics.

   (b) Show that product of two linear operators is a linear operator. 2

   (c) Without evaluating any integral, justify the following: 2+2

   (i) For n = 2 state, the probabilities of finding the particle in the *left half* and the *right half* of a one dimensional box are same.

   (ii) The relation of average values <A + B> = <A> + <B> holds true.

   (d) Show that if f is an eigenfunction of A with eigenvalue a then f will have the eigenvalue a^2 for operator A^2. What property of A you have assumed in your answer? 3

Unit-II

3. (a) State the difference between fluorescence and phosphorescence phenomenon with respect to the following: 4

(i) states involved in the process (ii) nature of transition (iii) position and intensity of spectra.

(b) For the photochemical reaction $A_2 \xrightarrow{h\nu} 2A$, the mechanism is as follows: 4

$$A_2 \xrightarrow{h\nu} A_2^*$$
$$A_2 \xrightarrow{k_2} 2A$$
$$A_2^* + A_2 \xrightarrow{k_3} 2A_2$$

Show that at low concentration of A_2, $\phi = 2$.

(c) Calculate the energy of 1 photon of light of wavelength 2450 Å. Will it be able to dissociate a bond in a diatomic molecule of energy 95 kcal/mol? 4

4. (a) A solution of substance *A* is irradiated with a light of λ = 3000 Å. The O.D. of solution is 0.398. If intensity of incident radiation is 1.5×10^{17} quanta s^{-1}, calculate the rate of formation of *B* in the reaction $2A \xrightarrow{h\nu} B + C$. Given: $\Phi = 0.48$. 4

(b) Find out the probability density of finding a 2*s*-electron of H atom (i) at the nucleus (ii) $r = 2a_0$ (iii) at $r = \infty$. Given $\psi_{2s} = \frac{1}{4\sqrt{2\pi}} a_0^{-3/2}\left(2 - \frac{r}{a_0}\right)e^{-r/a_0}$. 3+2

Hence draw the probability density vs. *r* plot for a 2*s* orbital.

(c) Show that at low concentration of absorbent, the intensity of absorbed radiation is directly proportional to concentration. 3

CEMAT-24-PB

Answer any *two* questions taking *one* from each unit

Unit-I

5. (a) How will the advancement of reaction (ξ) change for $N_2O_4(g) \leftrightharpoons 2NO_2(g)$ when (i) 5 mol of Ar introduced keeping mixture at constant P (ii) 5 mol of Ar introduced keeping mixture at constant V? 4

(b) Starting from $H = U + PV$, derive the expression 4

$$\left(\frac{\partial H}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V + V\left(\frac{\partial P}{\partial V}\right)_T.$$

(c) Calculate the change in free energy when 2 mol of H_2, 3 mol of O_2 and 5 mol of N_2 are mixed at 1 atm, 300 K. Gases behave ideally. Also calculate ΔG when the pressure of the mixture is increased to 5 atm. Calculate ΔS_{mix} and ΔH_{mix}. 3

(d) What is the dimension of fugacity coefficient (ϕ)? Will the fugacity coefficient be = +ve, –ve or zero for a real gas having intermolecular repulsive interactions? 2

6. (a) For the reaction: $2A + B \leftrightharpoons A_2B$, $\Delta G^0 = -1200$ cal mol^{-1} at 500 K. What total pressure is necessary to convert 60% of A into A_2B, where A and B are taken in the mole ratio 1:2? 4

   (b) Show that (i) $\left(\frac{\partial \mu_i}{\partial T}\right)_{P, n_{j\neq i}} = -\bar{S}_i$, (ii) $S = -\left(\frac{\partial A}{\partial T}\right)_{V,n}$ 2+2

   (c) For a reaction represented by $SO_2(g) + \frac{1}{2}O_2(g) \leftrightharpoons SO_3(g)$, $K_p = 1.7\times10^{12}$ at 300 K. Calculate K_p for $2SO_3(g) \leftrightharpoons 2SO_2(g) + O_2(g)$. 2

   (d) "Decrease in Helmoltz free energy is a measure of reversible isothermal work done by system." — Explain. 3

Unit-II

7. (a) In a 0.10 M solution of sodium acetate, calculate K_h, the degree of hydrolysis, and the pH at 298 K. [At 298 K, $K_w = 1.0\times10^{-14}$, $K_a = 1.8\times10^{-5}$]. 3

   (b) Construct an electrochemical cell for the reaction Ag (s) + ½ Br_2 (l)⇌AgBr (s). 2

   (c) Justify / Criticize (i) NH_2^- in liquid ammonia has abnormally high transport number (ii) In a conductometric titration concentration of the titrant is higher than the solution to be titrated. 4

   (d) 10 mL 0.1 N acetic acid solution is titrated with 0.1 N NaOH solution. Calculate the pH (i) initially (ii) at the half equivalence point (iii) at the equivalence point. Given K_a of acetic acid = 1.8×10^{-5}. 3

8. (a) Emf of a reversible cell is E at a temperature T. If E is not a function of temperature, find ΔS, ΔG and ΔH in terms of E. 3

   (b) If E^0 for $F_2 + 2e^- = 2F^-$ is 2.8 V, then what will be the E^0 for ½ $F_2 + e^- = F^-$? Justify your answer. 2

   (c) In a moving boundary experiment with 0.01N HCl, the boundary moved through a distance of 13.9 cm in a tube of diameter 1 cm on passing 11 mA current for 20 min. Find the transport number and mobility of H^+ ions. Given specific conductance of the solution is 10^{-2} ohm^{-1} cm^{-1}. 3

   (d) The activity solubility product of $CaCO_3$ is 4.8×10^{-9}. Find out the solubility of $CaCO_3$ in presence of a solution containing NaCl, and $MgCl_2$ each having 0.1 (M) concentration in solution. 4

WEST BENGAL STATE UNIVERSITY

B.Sc. Honours PART-II Examinations, 2018

CHEMISTRY-HONOURS

PAPER-CEMA-III

Time Allotted: 4 Hours | Full Marks: 100

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.

***Use separate answer scripts for* [CEMAT-23-IA & CEMAT-23-IB] and [CEMAT-23-OA & CEMAT-23-OB]**

Group-A

CEMAT-23-IA

Answer any *two* questions taking *one* from each Unit

Unit-I

1. (a) Account for the anomalous behaviour of the ionisation energies (kJ mol^{-1}) of Group 13 elements as given below: 3

B	Al	Ga	In	Tl
800	577	579	558	589

(b) Discuss the variation in properties of Group 14 elements with reference to 2+2+2

(i) Oxidation state. (ii) Electronegativity (iii) Metallic character

(c) (i) Explain why BCl_3 is mono-meric but $AlCl_3$ is a dimer. 2+2

(ii) $SiCl_4$ is hydrolysed easily whereas CCl_4 is resistant to hydrolysis– Justify.

2. (a) Write the structure of Thiosulfuric and Disulfuric acids and mention the oxidation state of Sulphur atoms in each compound. Discuss the hybridisation of central Sulphur for each case. 4

(b) Why does iodine show evidences of electropositive character? Cite two examples which prove the existence of electropositive iodine. 1+2

(c) What happens when $NaNH_2$ is treated with N_2O ? 2

(d) PCl_3 and NCl_3 hydrolyse in different mode– Explain giving equations. 2

(e) Explain with reasons why SF_6 is known but not SCl_6. 2

Unit-II

3. (a) Draw the qualitative M.O. energy level diagram of CN^-. Can CN^- act as an ambidentate ligand? Discuss in the light of M.O. theory. 3+2

(b) What do you mean by coordination position isomerism? Give an example to illustrate the definition. 1+1

(c) The fifth water molecule in $CuSO_4 \cdot 5H_2O$ is lost at a higher temperature than the other four molecules. Explain the observation. 2

(d) $[Cr(en)_2Cl_2]Cl$ is found in two forms, one violet and other green. On reaction with oxalate ion, the violet species produces corresponding oxalato derivative, while the green does not. Explain the result and write the IUPAC name of the oxalato derivative. 2+1

4. (a) Discuss the stereo-isomerism of co-ordination complexes having co-ordination number 4 with examples. 3

(b) Draw the qualitative M.D. energy level diagram of CO and calculate the bond order. 2+1

(c) What is the characteristic of semiconductors? Give one example. What is the basic difference between semiconductors and superconductors? 3

(d) State and explain two factors which determine N^- or O^- coordination of NO_2^-. 3

CEMAT 23-IB

Answer any *two* questions taking *one* from each Unit

Unit-I

5. (a) How does structure of boron nitride differ from that of graphite? 2

(b) The product of the reactions of diborane with ammonia depends on conditions of the experiment. – Explain with examples. 3

(c) Hydroxylamine can function both as oxidising and reducing agent. Explain and give appropriate examples. 1+2

(d) What are freons? Explain the effect of photolytic reactions of freons in the upper atmosphere. 1+2

(e) What happens when borazine is treated with HCl? Give equation. 2

6. (a) Give the method for preparation of straight chain and cross-linked silicones. Discuss how the uses of silicones are linked to their properties. 1+3

(b) Complete the following equations: 3

(i) $XeF_2 + SO_3 \rightarrow$ (ii) $XeF_2 + NO \rightarrow$ (iii) $XeF_4 + H_2O \xrightarrow{-80^\circ C} \rightarrow$

(c) Discuss the structure and bonding of ClF_3. 3

(d) What are NO_x? Discuss the role of freons in ozone layer depletion. 1+2

Unit-II

7. (a) Explain the significance of the principle of solubility product and common ion effect for the precipitation of iron, aluminum and chromium as hydroxides in qualitative analysis. 3

(b) Calculate the cell potential (E_{cell}) for the cell containing 0.1 (M) Ag^+ and 4.0 (M) Cu^{2+} at 25°C. ($E^0_{Cu^{2+}/Cu} = 0.34V$; $E^0_{Ag^+/Ag} = 0.80V$). 3

(c) What is Ellingham diagram? How can the thermodynamics of metallurgical processes be predicted from Ellingham diagram? 3

(d) $Mn^{2+}(aq.)$ is oxidised to MnO_4^- by sodium bismuthate in dil. HNO_3 medium. Balance the reaction by ion-electron method. 3

8. (a) Distinguish between disproportionation and comproportionation reactions. Explain why Cu (I) is not stable in aqueous solution. 2+1

[$E^0_{Cu^{2+}/Cu^+} = +0.15V$, $E^0_{Cu^{2+}/Cu} = +0.34V$].

(b) Calculate the S^{2-} ion concentration in a 0.25 (M) HCl solution saturated with H_2S at 25°C from the following data: 3+1

(i) Concentration of the saturated solution of H_2S at 25°C is 0.1(M)

(ii) The primary and secondary dissociation constants of H_2S are 9.1×10^{-8} and 1.2×10^{-15} respectively.

Hence, calculate the maximum concentration of Cd^{2+} which will remain in solution after precipitation as CdS under these conditions.

[$K_{sp}(cds) = 5.5\times10^{-25} g\,ion^2/L^2$].

(c) $E^0_{MnO_4^-/Mn^{2+}} = 1.51V$ and $E^0_{Cr_2O_7^{2-}/2Cr^{3+}} = 1.33V$. Calculate the pH at which these two couples will have the same reduction potential. 3

(d) The solubility product of ferric hydroxide is 1.1×10^{36} at 25°C. Calculate solubility of ferric hydroxide in g / L at this temperature. 2

Group-B

CEMAT-23-OA

Answer any *two* questions taking *one* from each unit

Unit-I

9. (a) How would you distinguish between the members in the following pairs of compound? 2×3

(i) N,N,2,6-tetramethylaniline and N,N,3,5-tetramethylaniline by UV spectroscopy.

(ii) Di-*tert*-butylketone and diethylketone by ^{1}H-NMR spectroscopy.

(iii) Acetylacetone and acetone by IR spectroscopy.

(b) An organic compound ($C_{10}H_{12}O_2$) has the following spectral data: 4

IR (cm^{-1}): 3050, 2950, 1730.

^{1}H-NMR (in ppm): δ 1.30(6H, d); 5.20(1H, m); 7.20(3H, m); 8.00 (2H, m).

Deduce the structure of the compound with the justification of the spectral data.

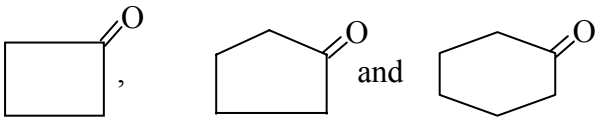
(c) Explain why acetic anhydride shows two carbonyl stretching frequencies in IR spectroscopy? 1.5

(d) In ^{1}H-NMR spectroscopy, a particular proton appears at 402 Hz downfield from TMS in a 180 MHz instrument. Calculate its δ-value. 1.5

10.(a) Which of the following nuclei are NMR active– Justify. 3

$^{2}D_{1}$ $^{14}N_{7}$ $^{12}C_{6}$ $^{31}P_{15}$ $^{16}O_{8}$ $^{19}F_{9}$

(b) Arrange the following cyclic ketones in increasing order of their carbonyl stretching frequency. Give reason for your answer. 2



(c) An organic compound with molecular formula C_3H_5OCl evolves CO_2 when added to aqueous $NaHCO_3$ solution. Its IR absorption shows a band at 1795 cm^{-1}. It gives a triplet and a quartet signals in its ^{1}H-NMR spectrum. Identify the compound. 3

(d) What in metastable peak in mass spectra? Explain with a suitable example. 2

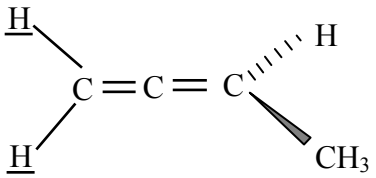
(e) Explain the following: 1.5+1.5

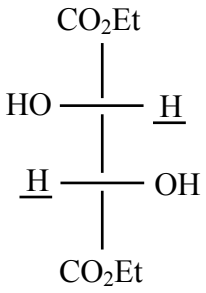
(i) C = C stretching frequency of cyclobutene appears at 1566 cm^{-1}, but that of 1-methylcyclobutene at 1641 cm^{-1}.

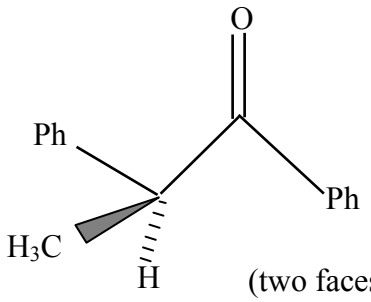
(ii) UV spectra of aniline and phenol are pH-dependent.

Unit-II

11.(a) Find out the topic relationship between the underlined H atoms and the mentioned faces in the following: 1×3

(i) 

(ii) 

(iii) 

(two faces of carbonyl)

Describe the process by which the relationships are determined.

(b) Explain what happens when ethyl acetoacetate is separately treated as follows: 3

(i) Treated with CH_3COCl and Mg;

(ii) First sodium salt of ethyl acetoacetate is formed and then treated with acetyl chloride.

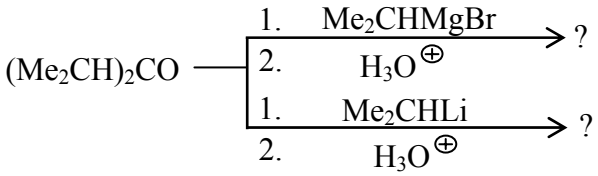
(c) Carry out the following transformations (any ***two***): 2×2

(i) Phenol to coumarin,

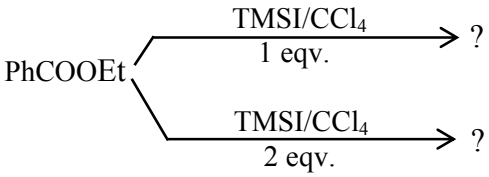
(ii) Hydroquinone to 1, 2, 4-trihydroxybenzene,

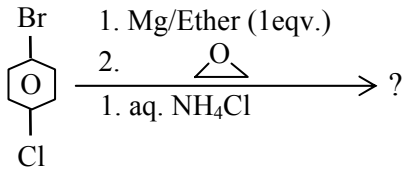
(iii) Phenol to *m*-nitrophenol.

(d) Complete the following reactions and justify the formation of product in each case. 2

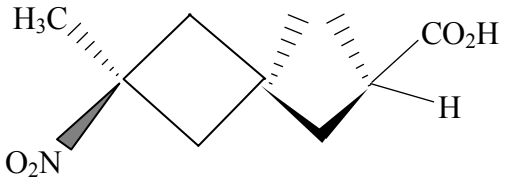


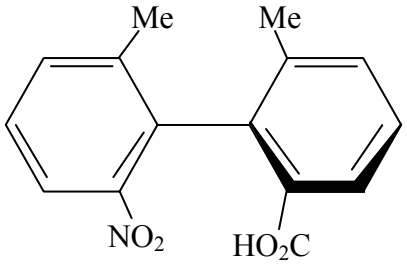
12.(a) Explain the formation of the products in the following reactions. 2×2

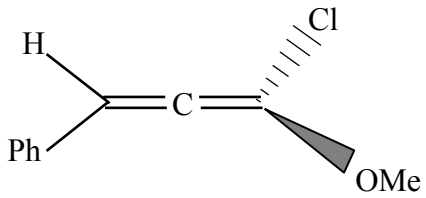
(i) 

(ii) 

(b) Assign R/S-configuration of the following compounds (any ***two***): 1.5×2

(i) 

(ii) 

(iii) 

Mention the relative priorities of different groups in each case.

(c) Fries rearrangement may be either inter- or intramolecular in nature. Give evidence in favour of the fact. 2

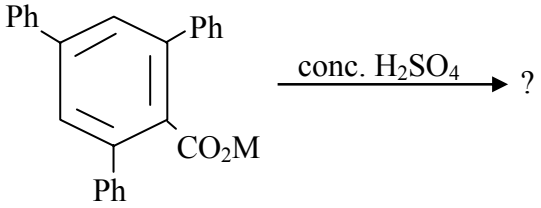
(d) A given sample of optically active 2-butanol shows the specific rotation of –6.76°. If pure (+)-2-butanol has the specific rotation of +13.52°, what is the molar ratio of two enantiomers in the given sample? 3

CEMAT-23-OB

Answer any *two* questions taking *one* from each unit.

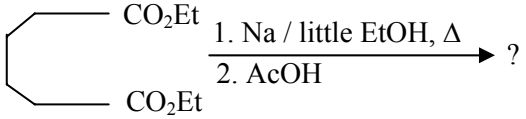
Unit-I

13.(a) Complete the following reactions giving mechanism (any ***three***): 3×3

(i) 

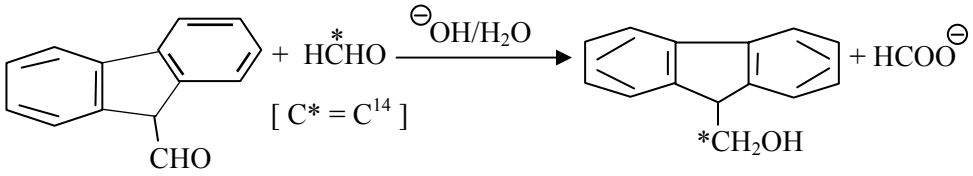
(ii) $RCHO + Al(OEt)_3 \longrightarrow ?$

(iii) $CH_3CHO + HCHO\ (excess) \xrightarrow{Ca(OH)_2} ?$

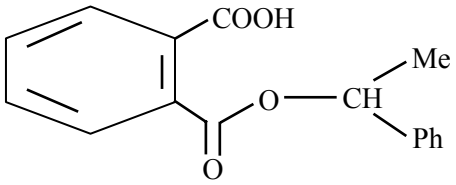
(iv) 

(b) Both *p*-dimethylaminobezaldehyde and *p*-nitrobenzaldehyde fail to undergo benzoin condensation but the mixture of these two undergoes the same condensation. Give the product with the explanation of its formation. 2

(c) Write down the mechanism of the following reaction. 2



14.(a) Alkaline hydrolysis of the optically active half ester given below, forms the racemic alcohol Ph(Me)CHOH. Explain with mechanism. 3



(b) How do you convert $PhCOCH_3$ to mandelic acid? Show the steps giving reagents and reaction conditions. 2

(c) Show the steps for the conversion of PhCHO to PhCDO. 2

(d) Arrange the following compounds in decreasing order of their rates of hydrolysis in alkaline medium and justify your answer. 2

(i) CH_3COCl (ii) CH_3CONH_2 (iii) $CH_3COOC_2H_5$

(e) In the Perkin reaction of PhCHO with Ac_2O and NaOAc, little styrene is obtained. — Explain. 2

(f) What happens when racemic lactic acid is heated? 2

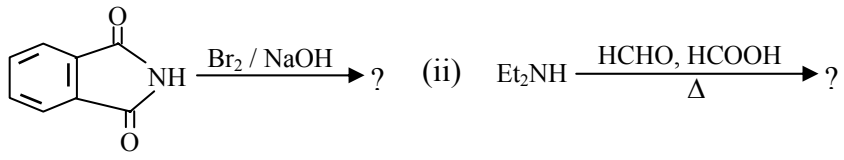
Unit-II

15.(a) State the action of $NaNO_2$ / HCl on: 3

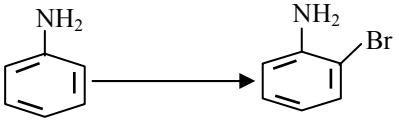
(i) N-methylaniline (ii) N, N-dimethylaniline and (iii) Benzylamine

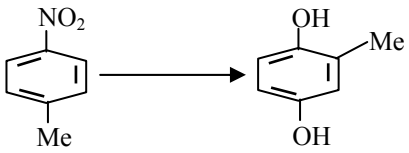
(b) How do you chemically distinguish between C_2H_5CN and C_2H_5NC? 2

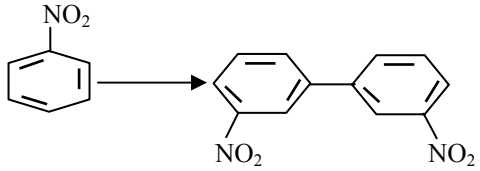
(c) Predict the products with plausible mechanism in the following reactions: 3



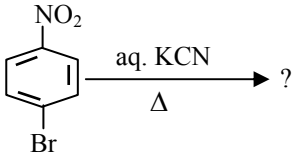
(d) Cary out the following transformations (any ***two***): 2×2

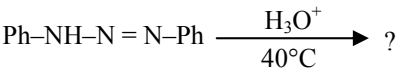
(i) 

(ii) 

(iii) 

16.(a) Give the product (s) formed in the following reactions giving plausible mechanisms. 2×2

(i) 

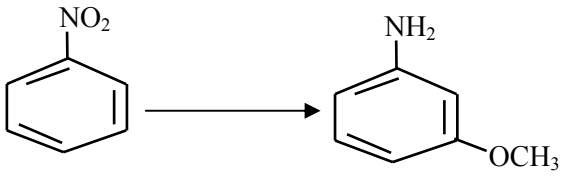
(ii) 

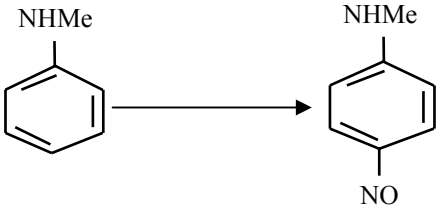
(b) Give an example of each of the following: 1+1

(i) Diazomethane acts as a 1, 3-diploar reagent.

(ii) Diazomethane acts as a base.

(c) Carry out the following conversions. 2×2

(i) 

(ii) 

(d) Predict the product in the following reaction. Give the probable mechanism. 2