

CHEMISTRY

(Paper II)

Time Allowed : Three Hours

Maximum Marks : 300

QUESTION PAPER SPECIFIC INSTRUCTIONS

(Please read each of the following instructions carefully before attempting questions)

There are EIGHT questions divided in two Sections.

Candidate has to attempt FIVE questions in all.

Question Nos. 1 and 5 are compulsory and out of the remaining, any THREE are to be attempted choosing at least ONE question from each Section.

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

Wherever any assumptions are made for answering a question, they must be clearly indicated.

Word limit in questions, wherever specified, should be adhered to.

SECTION 'A'

1. Answer any three of the following:

20×3=60

(a) The stereochemistry of nucleophilic substitution by the $S_{\text{RN}}1$ mechanism is almost always racemization. However the stereochemistry of substitution of A by thiophenoxide ion is dependent upon the concentration of nucleophile. When it is low, the product is almost racemic but when it is high, the product is of retained stereochemistry. Explain.

(b) Explain the mentioned pKa of the following compounds:

[Figure: Three amines with their pKa values: (i) quinuclidine (1-azabicyclo[2.2.2]octane, N at a bridgehead), pKa 10.58; (ii) the benzo-fused analogue in which one bridge of quinuclidine is a benzene ring, i.e. the bridgehead N is bonded directly to an aromatic carbon of a fused benzene ring (tricyclic, N in a bicyclo[2.2.2] cage), 7.79; (iii) N,N-dimethylaniline ($\text{C}_6\text{H}_5\text{NMe}_2$), 5.06]

(c) Explain the following observations with respect to yields of products:

[Figure: Two reactions of cyclopropyldiazonium ions with azide ion (N_3^- over the arrow). First: cyclopropyl- $^{15}\text{N}^+\equiv\text{N}$ (label 15 and the + charge on the N bonded to the cyclopropyl ring) $\rightarrow$ cyclopropyl- N_3 (3%) + cyclopropyl- $\text{N}^-(15)-\text{N}^+\equiv\text{N}$ (the 15 label on the N^- bonded to the ring) (97%). Second: cyclopropyl- $\text{N}^+\equiv^{15}\text{N}$ (+ on the N bonded to the ring, 15 label on the terminal N) $\rightarrow$ cyclopropyl- N_3 (23%) + cyclopropyl- $\text{N}^--^{15}\text{N}^+\equiv\text{N}$ (the 15 label on the middle N^+) (77%)]

(d) Halide A solvolyzes ten times faster than halide B. Both give C as the product of solvolysis in aqueous ethanol. Explain.

[Figure: A = bicyclo[2.2.1]hept-5-en-2-yl halide (norbornenyl halide) with X drawn exo; B = the same norbornenyl halide with X drawn endo (pointing down); C = tricyclo[2.2.1.0^{2,6}]heptan-3-ol (3-hydroxynortricyclene), HO on the carbon next to the cyclopropane ring]

2. (a)(i) Explain why the following 4 + 2 cycloaddition reaction does not occur to produce cantharidin isolated from dried beetles (*Cantharis vesicatoria*)

[Figure: Reaction scheme: furan + 2,3-dimethylmaleic anhydride $\rightarrow$ Diels-Alder adduct (7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride with CH_3 groups (H_3C , CH_3) on both C-2 and C-3, oxygen bridge at C-7) $\xrightarrow{-\text{H}_2/\text{Pd/e}}$ (as printed) $\rightarrow$ cantharidin (the saturated 7-oxabicyclo[2.2.1]heptane-2,3-dimethyl-2,3-dicarboxylic anhydride, labelled "Cantharidin")]

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(a)(ii) The order of reactivity of the following to solvolysis in 80% ethanol decreases in the same as they are written. Explain.

[Figure: (i) $(\text{CH}_3)_3\text{CBr}$; (ii) 1-bromoadamantane; (iii) 1-bromobicyclo[2.2.2]octane (Br at a bridgehead); (iv) 1-bromobicyclo[2.2.1]heptane (1-bromonorbornane, Br at a bridgehead)]

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(b) Explain the following observations: (i) Methyl vinyl ketone reacts more rapidly with cyclopentadiene than with 1, 3-butadiene in the cycloaddition reaction. (ii) Bromine reacts about 165 times faster with $\text{PhCH}=\text{CHPh}$ than with $\text{PhCH}=\text{CHBr}$. (iii) The following reaction proceeds 35 times less rapidly when $\text{R}=\text{CH}_3$ than when $\text{R}=\text{H}$:

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[Figure: Reaction: 1-bromo-4-nitro-3,5-dialkylbenzene (O_2N at C-4, Br at C-1, R groups at C-3 and C-5, i.e. both ortho to the nitro group) + piperidine (HN in a six-membered ring) $\rightarrow$ 1-(4-nitro-3,5-R₂-phenyl)piperidine (O_2N and the piperidin-1-yl group para, R groups ortho to NO_2)]

- (c) Indicate the steps by means of which you will effect the following conversions in good yields:

[Figure: Conversions: (i) 2-acetylfuran (furan-2-yl-COCH₃) $\rightarrow$ furan-2-yl-COCH=CH-CH₂-CH₃; (ii) acetophenone (C₆H₅COCH₃) $\rightarrow$ phenol (C₆H₅OH); (iii) cyclohexanone $\rightarrow$ 4,4a,5,6,7,8-hexahydronaphthalen-2(3H)-one (bicyclic octalone: C=O at C-2 conjugated with the C-1=C-8a ring-fusion double bond); (iv) cis-alkene (R and R on the same side, H and H on the same side, RHC=CHR) $\rightarrow$ trans-alkene (R and R on opposite sides)]

The only reagents available are m-chloroperbenzoic acid and triphenyl phosphine.

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- (d) Benzaldehyde on reaction with alcoholic $CN^\ominus$ gives benzoin but acetaldehyde under the same conditions does not give acetoin. Why? If you were to get acetoin, how will you proceed to synthesize it?

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3. (a) In the following reactions (i) and (ii), the major product of the reaction is A with very little amount of B. Rationalize the observations:

[Figure: (i) $CH_3COC(CH_3)_2CH_2CH_2Br$ (5-bromo-3,3-dimethylpentan-2-one) $\xrightarrow{\text{Base, Ether}}$ A: 3,3-dimethyl-2-methylenetetrahydrofuran (five-membered ring O-C(=CH₂)-C(CH₃)₂-CH₂-CH₂, H₂C= on the carbon next to O) + B: 2,2-dimethylcyclopentanone. (ii) $CH_3COC(CH_3)_2CH_2CH_2CH_2Br$ (6-bromo-3,3-dimethylhexan-2-one) $\xrightarrow{\text{Base, Ether}}$ A: 2,2-dimethylcyclohexanone + B: 3,3-dimethyl-2-methylenetetrahydropyran (six-membered ring O-C(=CH₂)-C(CH₃)₂-CH₂-CH₂-CH₂)]

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- (b) Give steps and reagents involved in the conversion of compounds written on the left hand side of the arrow to compounds written on the right hand side of the arrow:

[Figure: (i) cyclohexanone $\rightarrow$ 4-cyclohexylpentan-2-one (C₆H₁₁CH(CH₃)CH₂COCH₃); (ii) 2-methoxybenzoic acid (OMe and CO₂H ortho) $\rightarrow$ 2-heptylcyclohexanone (C=O with C₇H₁₅ on the adjacent ring carbon); (iii) cyclohex-2-en-1-one $\rightarrow$ cyclohexane-1,2,3-triol drawn as two stereoisomers: the first with all three OH on plain bonds, "and" the second with the C-2 OH on a hashed bond (OH at C-1 and C-3 plain); (iv) ethyl acetoacetate (CH₃COCH₂CO₂Et) $\rightarrow$ 3-methylcyclohex-2-en-1-one]

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- (c) Comment on the selectivity shown in the following reaction:

[Figure: 2-methyl-2-(3-oxobutyl)cyclopentan-1-one (cyclopentanone with CH₃ and CH₂CH₂COCH₃ on C-2) $\xrightarrow{\text{(i) Base, (ii) H}^+}$ bicyclic dione: 7a-methyl-hexahydro-1H-indene-1,5(4H)-dione (hydrindane with angular CH₃ at the ring fusion, C=O in the five-membered ring next to the quaternary ring-fusion carbon and C=O in the six-membered ring at C-5)]

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- (d) On heating A in toluene in the presence of SbF₅ and HF, one gets over 95% yields of p-nitro toluene. Explain the mechanism of the reaction.

[Figure: A = 9-nitroanthracene (NO_2 on the central ring carbon C-9)]

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4. (a) How will you prove that Beckmann rearrangement is an intermolecular rearrangement? Take suitable examples to illustrate your answer.

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- (b) Give the mechanism of the reaction that explains the following observations: Explain your answer.

[Figure: Isoprene (2-methyl-1,3-butadiene) + methyl vinyl ketone (CH₂=CHCOCH₃) $\rightarrow$ 1-(4-methylcyclohex-3-en-1-yl)ethanone (acetyl and the ring-double-bond methyl in 1,4-"para" relationship) + second product drawn as 1-(3-methylcyclohexyl)ethanone (acetyl and methyl 1,3 on a cyclohexane ring; no ring double bond drawn). Yields: (i) Heat in a sealed tube at 120 °C: 71% and 29%; (ii) Keep in contact with SnCl₄·5H₂O at 0 °C: 93% and 7%]

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- (c) Explain why A reacts with sodium ethoxide to give B, but with sodium acetate and sodium phenoxide, it gives C and D respectively.

[Figure: A = β-propiolactone (oxetan-2-one: four-membered ring -CH₂-CH₂-C(=O)-O-); B = ⁻OCH₂CH₂CO₂C₂H₅; C = CH₃COOCH₂CH₂CO₂⁻; D = PhOCH₂CH₂CO₂⁻]

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- (d)(i) How do you explain the concepts of aromaticity, anti-aromaticity and homo-aromaticity?

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- (d)(ii) Which of the following compounds are aromatic and why?

[Figure: A = cycloheptatrienyl anion (seven-membered ring with three C=C and a $\ominus$ charge on the sp³ carbon); B = cyclooctatetraene; C = tropone (cyclohepta-2,4,6-trien-1-one); D = pentalene (two fused five-membered rings, four C=C); E = azulene (fused five- and seven-membered rings)]

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SECTION 'B'

5. Answer any three of the following:

20×3=60

(a) Normal O - H stretch comes at about 3600 cm^{-1} . What is the reduced mass for O - H? What happens to the reduced mass when atomic mass of each atom is doubled in turn; i.e., when O - H is converted to O - D and S - H? In fact both O - D and S - H stretch come at about 2500 cm^{-1} . Why?

(b) Indicate how IR spectrum can be used to distinguish:

[Figure: (i) 1-(cyclopent-1-en-1-yl)ethanone (acetyl on the ring double-bond carbon, conjugated) and 1-(cyclopent-3-en-1-yl)ethanone (acetyl on the sp^3 ring carbon opposite the $C=C$, non-conjugated), each drawn with $C(=O)CH_3$; (ii) dicyclohexylidenemethane (two cyclohexane rings joined by $=C=$, an allene) and bis(cyclohex-1-en-1-yl)methane (two cyclohexene rings joined through their double-bond carbons by CH_2)]

(c) Indicate how NMR can be used to distinguish

[Figure: (i) 3-chlorotoluene, 2-chlorotoluene and 4-chlorotoluene (CH_3 and Cl meta, ortho and para); (ii) benzyl bromide ($C_6H_5CH_2Br$), 2-bromotoluene (Br and CH_3 ortho) and 3-bromotoluene (Br and CH_3 meta)]

(d) Syn diol A can be converted to trans olefin B in good yields. Write all the steps involved in such a conversion. Give reasons for your choice of method or the reagents.

[Figure: A = $R_1CH(OH)CH(OH)R_2$ drawn in zig-zag with one OH up and one OH down (the syn diol); B = trans- $R_1CH=CHR_2$]

6. (a) Explain how can A be converted to B on treatment with silver perchlorate in methanol.

[Figure: A = 2,3,4,6-tetra-O-acetyl glucopyranosyl bromide drawn in chair form: AcO on C-6 (CH_2OAc), C-4 and C-3, the C-2 acetoxy group ($O-C(=O)-CH_3$) drawn axial-down, and Br at C-1 axial-down (α -bromide), ring O; B = the corresponding methyl glycoside with OCH_3 at C-1 equatorial (β), AcO at C-6, C-4, C-3 and the C-2 $O-C(=O)-CH_3$ group drawn down]

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(b) How can one identify from the inspection of mass spectrum of the compound that it contains (i) one nitrogen atom (ii) one chlorine atoms (iii) two chlorine atoms (iv) one bromine atom

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(c) Outline the synthesis of 100% cis-poly(isoprene). Discuss reasons for the choice of reagents or catalysts and the mechanism of polymerization.

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7. (a) The natural product bullatenone was isolated in the 1950s and assigned the structure A. When compound A was synthesized, it was not identical with the natural sample. Predict the expected ^1H NMR spectrum of A. Given the full spectroscopic data available nowadays, but not in 1950s, say why A was wrong and suggest a better structure for bullatenone.

[Figure: A, "Alleged bullatenone": 3-methyl-6-phenyl-2,3-dihydro-4H-pyran-4-one (six-membered ring: C-4 $C=O$, C-5=C-6 double bond with Ph on C-6, ring O, C-2 CH_2 , C-3 bearing a CH_3)]

Spectra of bullatenone: Mass spectrum: m/z 188 (10%), Mol. formula: ($C_{12}H_{22}O_2$), 105 (20%), 102 (100%), 77 (20%) IR spectrum: 1604 and 1705 cm^{-1} ^1H NMR spectrum: 1.45(6H, s), 5.82(1H, s) 7.35(3H, m), 7.68(2H, m)

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(b)(i) Sketch the high resolution H NMR spectrum of ethyl acetoacetate.

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(b)(ii) Indicate main stretch frequencies for functional groups present in acetyl acetone. What would happen to the spectrum if a small amount of organic base is added to it?

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(c) Illustrate Woodward-Fieser Rules to calculate the expected λ_{max} of enones in the uv-spectrum.

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8. (a) Give the steps involved in the synthesis of the following compounds from indicated materials: (i) Phenolphthalein from phenol, phthalic anhydride and sulphuric acid. (ii) α -methyl cinnamic acid from benzaldehyde, base and propanoic anhydride.

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(b) Using chemical and/or spectral methods (as indicated), show how the following can be differentiated: (i) $HC\equiv CCH_2CH_2OH$ and $CH_3C\equiv CCH_2OH$ (Chemical methods only) (ii) (Chemical and spectral methods) (iii) (Spectral methods only)

[Figure: (ii) 2-phenylpropan-2-ol ($C_6H_5C(CH_3)_2OH$) and (2,4-dimethylphenyl)methanol (benzene ring with CH_2OH at C-1, CH_3 at C-2 and H_3C at C-4); (iii) 2-hydroxyacetophenone (OH and $COCH_3$ ortho) and 4-hydroxyacetophenone (OH and $COCH_3$ para)]

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(c) Illustrate different types of pericyclic reactions by taking at least one example for each type. Explain why some of these reactions are also occasionally referred to as 'no reagent' reactions.

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(d) There are two possible products from Favorskii rearrangement that occur, when A reacts with sodium methoxide. What are the products and which will be formed in larger amount?

[Figure: A = $\text{PhCH}_2\text{C}(=\text{O})\text{C}(\text{Cl})(\text{CH}_3)_2$, printed as "Ph CH₂ C(=O)—C(Cl)—(CH₃)₂" (1-chloro-1,1-dimethyl... i.e. 3-chloro-3-methyl-1-phenylbutan-2-one)]

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