Civil Services (Main) Examination, 2003

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) (i) Which of the following compounds are aromatic? Give reasons to justify your answer: (ii) On the basis of modern concept of aromaticity how will you explain azulene as blue and shows dipole, moment of 0.8 D whereas its isomer naphthalene is colourless and has no dipole moment?

[Figure: (i) six structures: I – a 1,2-dithiole ring (five-membered ring S–S with one ring C=C) whose ring carbon next to S carries an exocyclic C=CH–CH=S chain, the terminal S drawn next to (not bonded to) the ring S (thiathiophthene-type, "S–S⋯S"); II – four-membered ring (rectangle) with one C=C (top side) and a ⊕ charge on each of the two lower carbons (cyclobutadiene dication); III – eight-membered ring with three C=C drawn and two ⊖ charges on adjacent lower carbons (cyclooctatetraene dianion); IV – peri-fused tricyclic C_{13} hydrocarbon (phenalene skeleton: three six-membered rings sharing a central carbon) with six C=C drawn around the periphery; V – mesoionic sydnone: five-membered ring R–N(+)–CH=C(–O⊖)–O–N, i.e. R on N-3, CH (C-4), C-5 bearing $O^{\ominus}$, ring O-1 and N-2, with a dashed circle containing "+" in the ring; VI – naphthalene skeleton with one ring benzenoid and the other ring having only one further C=C, i.e. 1,2-dihydronaphthalene [?]]

(b) Provide mechanism for the following reactions:

[Figure: (i) bicyclo[3.2.0]hept-2-ene (cyclopentene fused to cyclobutane) bearing on the cyclobutane carbon C-7 an OAc and an H, and on C-6 a D and an H (stereochemistry as drawn: OAc and D on wedge-type bonds, H on the other bonds) –Δ, 300°C→ bicyclo[2.2.1]hept-2-ene (norbornene) bearing OAc on one carbon of the saturated two-carbon bridge (with H) and D on the adjacent carbon (with H), the stereochemistry being shown (1,3-sigmatropic shift); (ii) 2-methoxytropone (cyclohepta-2,4,6-trien-1-one with CH_3O on C-2) –hν→ ? –hν→ 7-methoxybicyclo[3.2.0]hept-6-en-2-one (cyclopentanone fused to a cyclobutene; C=O on the five-membered ring adjacent to a ring-junction carbon; OCH_3 on the cyclobutene double-bond carbon next to that junction)]

(c) Suggest a method for the synthesis of the following compounds using the given reaction

[Figure: (i) ethyl 3-phenylbut-2-enoate, C_6H_5−C(CH_3)=CH−COOEt – "using Reformatsky reaction" (printed "Reformatsky" garbled); (ii) ethyl 1-methylnaphthalene-2-carboxylate (naphthalene with CH_3 at C-1 and COOEt at C-2) – "using Stobbe reaction"; (iii) 4-methylfuran-2-carboxylic acid (furan with COOH on C-2 and CH_3 on C-4) – "using Reimer-Tiemann reaction"]

(d) Rationalise the products formed in the following reactions:

[Figure: (i) 1,2-dimethylcyclohexane-1,2-diol in chair form (C-1: OH axial up, CH_3 equatorial; C-2: HO equatorial, CH_3 axial down) –aq. H_2SO_4→ 2,2-dimethylcyclohexanone in chair form (C-2 bearing axial CH_3 up and equatorial CH_3; C=O on the adjacent carbon); (ii) 1,2-dimethylcyclohexane-1,2-diol in chair form (C-1: OH axial up, CH_3 equatorial; C-2: CH_3 equatorial, OH axial down) –aq. H_2SO_4→ 1-acetyl-1-methylcyclopentane (cyclopentane C-1 bearing CH_3 and $COCH_3$); (iii) 1-chlorocyclohexyl phenyl ketone (cyclohexane C-1 bearing Cl and COC_6H_5) –NaOEt, Ethanol→ ethyl 1-phenylcyclohexanecarboxylate (C-1 bearing COOEt and C_6H_5)]

2. (a) How would you explain the addition of HI to tiglic acid (A) and angelic acid (B) to give stereospecifically the erythro-and threo-β-iodo acids, (C) and (D) respectively instead of a mixture of both the acids (C and D) in each case **20**

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[Figure: Cis, (A): alkene drawn with Me (upper left), Me (lower left), COOH (upper right), H (lower right) –HI, $CHCl_3$→ Erythro, (C): Newman projection, front carbon bearing Me (upper left), COOH (upper right), H (down); rear carbon bearing I (up), Me (lower left), H (lower right). Trans, (B): alkene drawn with Me (upper left), H (lower left), COOH (upper right), Me (lower right) –HI, $CHCl_3$→ Threo, (C) (label as printed): Newman projection, front carbon bearing Me (upper left), COOH (upper right), H (down); rear carbon bearing I (up), H (lower left), Me (lower right)]

(b) Predict the formation of major and minor products in the following reactions and also indicate the name through which they are associated. Show the mechanism of their formation.

[Figure: (i) chair cyclohexane: C-1 bearing O–CS–SMe (equatorial), C-2 bearing Me (equatorial), C-6 bearing C_6H_5 (axial, up) –Δ→ ? + ?; (ii) the same chair with O–CS–SMe at C-1 (equatorial) and Me at C-2 (equatorial) but C_6H_5 at C-6 axial, down –Δ→ ? + ?] **20**

(c) (i) "A 2πS + 2πS cycloaddition reaction is thermally forbidden while it is photochemically allowed". Explain by writing the symmetry correlation diagram. (ii) Give the structure of the product(s) in the following reactions showing mechanism.

[Figure: hexa-1,5-dien-3-ol (CH_2=CH−CH(OH)−CH_2−CH=CH_2, HO on the carbinol carbon) –Δ→ ; 2-methoxybuta-1,3-diene (CH_3O on C-2) + acrylonitrile (CH_2=CH−CN) –Δ→] **20**

3. (a) With suitable mechanism explain how optically active cis-2-acetoxycyclohexyl tosylate (A) on heating with acetic acid and K-acetate gives the optically active transdiacetate (B) with a slow rate whereas its optically active trans isomer (C) furnishes the optically inactive trans-diacetate.

[Figure: (A) chair cyclohexane with OTs axial (up) on C-1 and OAC equatorial on the adjacent C-2 –KOAC, HOAC→ (B) chair with OAC on C-1 and OAC on C-2 (both drawn equatorial). (C) chair with OTs axial up on C-1 and OAC axial down on C-2 –KOAC, HOAC→ (D) chair with OAC axial up on C-1 and OAC axial down on C-2 & (D) chair with both OAC equatorial on C-1 and C-2] **20**

(b) The optically active Ketone (A) undergoes recemisation on treatment with NaOEt as well as dil. H_2SO_4. Explain the observation with mechanism.

[Figure: (A) 2-methylcyclopentanone with H on a wedge and CH_3 on a hashed bond at C-2] **20**

(c) (i) In the reaction shown below with (A), the product isolated is (B) and not (C). Explain the reason with mechanism. (ii) Give the name and stereochemistry of the product in the following transformation from A→B.

[Figure: (i) pyrrole (A) –CH_3−COCl, An. $AlCl_3$→ (B) 3-acetylpyrrole ($COCH_3$ on C-3) + (C) 2-acetylpyrrole ($COCH_3$ on C-2); (ii) Trans, cis, trans-2, 4, 6-octatriene (A) (drawn U-shaped with the terminal CH_3 groups pointing outward and the two inner terminal H atoms pointing inward) –disrotatory cyclisation→ (B)] **20**

4. (a) The threo-3-phenyl-2-butylamine (A) undergoes deamination with nitrous acid in acetic acid and gave the following results:

[Figure: (A) Newman projection: front carbon bearing NH_3 (as printed; up), CH_3 (lower left), H (lower right); rear carbon bearing C_6H_5 (down), CH_3 (upper left), H (upper right) –HNO_2, CH_3COOH→ C_6H_5−CH(OAC)−$CH(CH_3)_2$ 32% + C_6H_5−CH(CH_3)−CH(CH_3)−OAC 44% (mixture of threo and erythro acetate) + C_6H_5−C(CH_3)(OAC)−CH_2−CH_3 24%]

Interprete the observation. **20**

(b) Suggest the possible mechanism for the conversion of 2, 6-dimethyl phenyl allyl ether (A) to 4-allyl-2, 6-dimethyl phenol (B). How will you prove that it passes through a dienone intermediate?

[Figure: (A) 2,6-dimethylphenyl allyl ether, O−CH_2−CH=CH_2 on C-1 with CH_3 on C-2 and C-6 –Δ→ (B) 4-allyl-2,6-dimethylphenol (OH on C-1, CH_3 on C-2 and C-6, CH_2−CH=CH_2 on C-4)] **20**

(c) The transformation of hydrazobenzene (A) to benzidine (B) in the presence of acids is considered to be an intermolecular rearrangement. How will you verify it by cross-over experiment?

[Figure: C_6H_5−NH−NH−C_6H_5 (labelled (B) as printed) –H^+→ H_2N−C_6H_4−C_6H_4−NH_2 (4,4′-diaminobiphenyl, benzidine) (B)] **20**

SECTION 'B'

5. Answer any THREE of the following:

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(a) Give the reaction and show the structure of the polymer products formed from the following monomers: $(CH_3)_2SiCl_2$ and CH_3SiCl_3 What will be the geometry of these polymers? How are these polymers used?

(b) Predict the product(s) in the reactions given below with mechanism wherever possible.

[Figure: (i) tetralin (1,2,3,4-tetrahydronaphthalene) $-CrO_3$, ACOH→ ; (ii) 3-methylthiophene –NBS, Pyridine / Peroxide→ ; (iii) cyclohex-2-en-1-ol $-OsO_4$ [?], Pyridine / THF [?] (printed "CHF")→ ; (iv) methyl 3-oxohex-4-enoate, $CH_3-CH=CH-CO-CH_2-COOCH_3$, with two arrows: $-NaBH_4$, CH_3OH→ and $-LiAlH_4$, ether→]

(c) Write the structure of the product(s) in the following reactions with mechanism:

[Figure: (i) $CH_3-CO-CH_2-CH_2-CH(CH_3)_2$ –hν→ ; (ii) butanal ($CH_3CH_2CH_2CHO$) + 2-methylbut-2-ene ($(CH_3)_2C=CH-CH_3$) –hν→ ; (iii) a bicyclic cyclopropyl ketone: carbocyclic ring fused to a cyclopropane, drawn in perspective, with a benzoyl group $C(=O)-C_6H_5$ on a cyclopropane ring-fusion carbon [?] –hν→ ; (iv) 2 × trans-2-butene ($CH_3-CH=CH-CH_3$, methyls trans) –hν→]

(d) Deduce the structure of the compound from the following spectral data assigning reason for each peak: IR(cm^{-1}): 2875, 1720, 1622, 1310, 725 ^1H NMR (δ): 1.23 (S, 3 H), 4.25 (S,2 H), 7.2 (m, 5 H) Mass (m/z): 138, 96, 91, 65, 43 Molecular formula: $C_9H_{10}O_2$.

6. (a) What are phosphazene polymers? How a phosphazene polymer having $-O-CH_2-CF_3$ group is prepared? What are its important surgical uses? **20**

(b) (i) Calculate the λ_{max} for the following using Wood ward-Fieser rule: (ii) Account for the changes in the carbonyl stretching frequency in the following.

[Figure: (i) (1) bicyclic α,β-unsaturated ketone: 4a-methyl-4,4a,5,6,7,8-hexahydronaphthalen-2(3H)-one skeleton with angular CH_3 at C-4a, C=O at C-2, C=C between C-1 and C-8a, a CH_3 on C-1 and an isopropyl group on C-7; (2) tricyclic tetraene: hydrophenanthrene skeleton with an angular CH_3 at the junction of the left and middle rings, one C=C in the left ring (conjugated with the middle ring), two C=C in the middle ring, and one C=C in the right ring at the ring junction side, forming a conjugated system; (ii) three five-membered lactones: furan-2(5H)-one (C=C between C-3 and C-4, α,β-unsaturated) $\nu_{C=O}$: 1750 cm^{-1}; γ-butyrolactone (saturated) 1770 cm^{-1}; furan-2(3H)-one (C=C between C-4 and C-5, next to the ring O) 1800 cm^{-1}] **20**

(c) (i) How will you account for the following mass spectral peaks in $C_6H_5-CH_2-OH$? (m/z): 108, 107, 106, 105, 91, 79. Show the fragmentation pattern. (ii) The rotational spectrum of HCl molecule shows that the rotational lines are equally separated by 2070 cm^{-1}. Calculate the internuclear bond length. (h=6.63×10^{-34} Js, N_a=6.023×10^{23}). **20**

7. (a) 1000 g. of a polymer of molecular weight 1000 g/ mole was mixed with 1000 g of another polymer of molecular weight 10^6 g/mole. Calculate the ratio of the weight average molecular weight to number average molecular weight of the mixed polymer **20**

(b) Suggest suitable reagents for the synthesis of the following

[Figure: (i) cyclohexane-1,2-dione from cyclohexanone; (ii) 3-(but-3-enyl)cyclohexan-1-ol (cyclohexanol with $CH_2CH_2CH=CH_2$ at C-3) from 3-(2-bromoethyl)cyclohexan-1-ol (cyclohexanol with CH_2-CH_2Br at C-3); (iii) 1-methylcyclopentan-1-ol from 1-methylcyclopentene; (iv) 2,4-dimethylpyrrole (CH_3 on C-2 and C-4 of 1H-pyrrole) from $CH_3-CO-CH_2-NH_2$] **20**

(c) (i) Name the various types of ultramarines. Give their composition and uses. (ii) Rationalise the following transformations:

[Figure: (A) 2-vinylbicyclo[2.2.2]octan-2-ol skeleton drawn in perspective (bicyclo[2.2.2] cage, the carbon bearing OH and a vinyl group $CH=CH_2$; ring C=C not clearly shown [?]) –THF, reflux→ (B) cis-octalone: 3,4,4a,5,6,8a-hexahydronaphthalen-2(1H)-one type bicyclic ketone with both ring-junction H on dashed bonds (cis), C=O in one ring and a C=C in the other ring adjacent to a ring-junction carbon; (C) 6-vinylbicyclo[3.1.0]hex-2-ene (cyclopentene fused to a cyclopropane, the cyclopropane carbon bearing H and a vinyl group) –heat→ (D) bicyclo[3.2.1]octa-2,6-diene] **20**

8. (a) (i) Free radical polymerisation of 1, 3-butadiene gives a polymer containing $-CH_2-CH=CH-CH_2-$ and $-CH_2-CH(CH=CH_2)-$ units, the exact Proportion of which depends on temperature. How will you account for this observation? (ii) "Natural rubber is elastic whereas gutta percha is highly crystalline and rigid though both are formed from the same monomer." Give reasons. **20**

(b) (i) How will you explain the formation of m/z = 149 in the mass spectrum of diethylphthate? Show the fragmentation pattern to show it. (ii) Suggest reactant, reagent and mechanism for **20**

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the synthesis of B from A.

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