Civil Services (Main) Examination, 2009

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:

(a) What are the products from ozonolysis of ortho-xylene after treatment with Zn? **20**

(b) (i) What kind of substitution on benzene ring stabilizes the phenyl carbanion and where is it most effective? Explain mechanistically. (ii) Which has higher dipole moment between and and why?

[Figure: (ii) first compound: sesquifulvalene — a cyclopentadiene ring (two ring C=C) joined by an exocyclic C=C to a cycloheptatriene ring (three ring C=C), i.e. cyclopentadienylidene=cycloheptatrienylidene; "and"; second compound: 6,6-dimethylfulvene — cyclopentadiene ring with exocyclic $=C(CH_3)_2$] **20**

(c) Pyridine follows nucleophilic substitution easily but not electrophilic. Explain mechanistically. **20**

(d) What are the catalyst(s) for the following chemical reactions? (i) Aldol condensation (ii) Claisen condensation (iii) Perkin reaction (iv) Fries rearrangement (v) Pinacol-pinacolone rearrangement **20**

2. (a) Fusion of with $NaNH_2$ gives two derivatives (m & p). Explain mechanistically.

[Figure: benzene ring bearing CH_3 and Cl para to each other (4-chlorotoluene)] **15**

(b) Optically active $C^*(CH_3)(Br)(H)(C_2H_5)$ on refluxing in polar solvent like THF or DMF recemizes but it does not occur in cyclohexane. Explain.

[Figure: 2-bromobutane drawn as a stereocentre C marked with an asterisk, bearing CH_3, Br, H and C_2H_5] **15**

(c) For conversion of C_6H_6 to C_6D_6 using excess DCl, the used catalyst is one of the following. Identify it and justify with mechanism: (i) H_2SO_4 (ii) Pd (iii) Pt (iv) Ni. **15**

(d) The addition of Br_2 to $CH_2{=}CH_2$ in presence of excess Cl^- produces $Br{-}CH_2{-}CH_2{-}Cl$ as one of the products. Explain mechanistically. **15**

3. Identify the intermediates and products in the following reactions:

(a) $CH_3{-}CO{-}C_6H_5 \rightarrow \underset{\text{b) HCl}}{\overset{\text{a) Mg}}{}} A \rightarrow \underset{\text{reflux}}{\overset{H^+}{}} B \rightarrow \underset{\text{b) acid}}{\overset{\text{a) } I_2+NaOH}{}} C+D$ **12**

(b) $CH_2{=}CH{-}CH{=}CH_2+SO_2 \rightarrow A \rightarrow \underset{}{\overset{NaBH_4}{}} B \rightarrow \underset{\text{heat}}{\overset{Pd}{}} C$

[Figure: diene drawn as skeletal 1,3-butadiene] **9**

(c) $\rightarrow \overset{OBr^-}{} A \rightarrow \overset{NaNO_2+HCl}{} B \rightarrow \underset{\text{+ alkalic}}{\overset{\text{m-Cresol}}{}} C \rightarrow \overset{Na_2S_2O_4}{} D+E$

[Figure: starting compound: benzene ring bearing $CONH_2$ and CH_3 para to each other (4-methylbenzamide)] **15**

(d) $C_6H_6+CH_2{=}CH{-}CH_3 \rightarrow \overset{AlCl_3}{} A \rightarrow \underset{\text{heat}}{\overset{O_2}{}} B \rightarrow \overset{H_3PO_4}{} C+D$ **12**

(e) $\rightarrow \underset{\text{heat}}{\overset{AlCl_3}{}} A \rightarrow \underset{HCl}{\overset{Zn(Hg)}{}} B$

[Figure: benzene ring bearing $O{-}CO{-}(CH_2)_4{-}CH_3$ and, meta to it, OH (3-hydroxyphenyl hexanoate)] **6**

English version compiled from published transcriptions and cross-checked across sources; not a facsimile of the official UPSC question paper.

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(f) $\rightarrow \overset{NaNO_2}{\underset{HCl}{}} A \rightarrow \overset{HBr}{\underset{CuBr}{}} B$

[Figure: benzene ring bearing NH_2 and CH_3 para to each other (4-methylaniline)] **6**

4. (a) Explain the following transformation through mechanism.

[Figure: Camphene Chloride (camphene hydrochloride): bicyclo[2.2.1]heptane with C2 bearing Cl and CH_3 and C3 bearing two CH_3 groups → bornyl/isobornyl chloride: bicyclo[2.2.1]heptane with two CH_3 on the C7 bridge, CH_3 on bridgehead C1 and Cl on C2 (1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl chloride)] **20**

(b)(i) Identify the products in following reactions: $CH_3CH_2CHO + CH_2O \rightarrow \overset{\text{mild alkali}}{\underset{\text{reflux}}{}} A \rightarrow \overset{H_3BO_3}{} B$

[Figure: (i) first reactant drawn as $CH_3CH_2C(=O)-H$] **8**

(b)(ii) $\rightarrow \overset{CHCl_3/KOH,\ reflux}{\underset{\text{Acidify, steam distil}}{}} C \rightarrow \overset{(CH_3CO)_2O}{\underset{CH_3COONa,\ reflux}{}} D$

[Figure: starting compound phenol (benzene ring with OH)] **8**

(b)(iii) $\rightarrow \overset{SeO_2}{} E \rightarrow \overset{CrO_3}{} F \rightarrow \overset{heat}{\underset{\text{in alkaline medium}}{}} G \rightarrow \overset{CN^-}{\underset{Catalyst}{}} H$

[Figure: starting compound acetophenone ($C_6H_5-CO-CH_3$, drawn as benzene ring with $C(=O)CH_3$)] **16**

(b)(iv) $(COOEt)_2 + CH_3CO_2Et \rightarrow \overset{NaOEt}{\underset{Acidify}{}} I \rightarrow \overset{BrCH_2COOEt}{\underset{Zn}{}} J$ (diethyl oxalate drawn as COOEt–COOEt) **8**

SECTION 'B'

5. Answer any three of the following:

(a) (i) Nylon 6 can be produced from a monomer. What is that monomer and what is the mechanism of polymerization? (ii) Phenol condenses with formaldehyde in acidic medium. What is the mechanism of condensation? **20**

(b) (i) The presence of P + 1 peak (P = parent peak) in mass spectra of organic compounds may be attributable to natural abundance of some isotopes. What are those isotopes? (ii) Write numbers of major peaks in ^1H NMR spectra of the following compounds:

[Figure: 1. $(CH_3)_2C=CH_2$ (2-methylpropene); 2. $CH_3(Cl)C=CH_2$ (2-chloropropene); 3. $H(Br)C=CH_2$ (vinyl bromide); 4. methylcyclopropane drawn as a triangle: one ring carbon with H (up) and H (dotted, down), one ring carbon with CH_3 (up) and H (dotted, down), the third ring carbon with H (up, inside the ring) and H (dotted, down)] **20**

(c) (i) Proton NMR of $Cl-CH_2-CH_2Cl$ shows only one signal whereas $Cl-CH_2-CH_2-Br$ shows more than one signal. Explain. (ii) p-hydroxy acetophenone is mixed with D_2O (very excess) in mild alkaline condition. The mass spectra of final product (parent peak) will differ from parent peak of p-hydroxy acetophenone. What is the difference in unit of mass? **20**

(d) (i) DNA precipitates with cationic polymer but not with anionic polymer. Explain. (ii) Acid hydrolysis of Nylon 6 is faster than acid hydrolysis of polyester. Explain with mechanism. **20**

6. (a) (i) Write products for photochemical dissociation of 2-pentanone. Write the possible intermediate. Identify A and B (ii) Write products of photochemical oxidation of following:

[Figure: (i) N-chloro-N-methylpentylamine drawn in a pseudo-ring (chair-like) conformation: N bearing Cl and CH_3 attached to a five-carbon chain whose terminal (δ) carbon, drawn next to N without a bond, carries the H shown –(H^+, hν)→ A –(NaOH)→ B; (ii) (E)-4-methylpent-2-ene ($CH_3-CH=CH-CH(CH_3)_2$, the tertiary allylic H drawn explicitly) and anthracene] **20**

(b)(i) H^+ ion shifts $n \rightarrow \pi^*$ transition of >C=O to higher energy. Explain. **12**

(b)(ii) Which reagent can be used to convert $CH_3-CH=CH-CH_2-CO_2Me$ to $CH_3-CH=CH-CH_2-CH_2OH$. **6**

(c)(i) Polar solvent shifts λ_m of $\pi \rightarrow \pi^*$ transition of >C=O to higher value. Explain. **12**

(c)(ii) Ethene and Ethyne unlike propene and propyne do not give C to C multiple bond stretching bonds in their IR spectrum. Explain. **10**

7. (a) Write equation for the formation of glyptal resin? How can it be made softer? **20**

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(b) Write monomer of Teflon. How is the monomer synthesized? **10**

(c) In ^{1}H NMR spectra C_2H_2 and CF_3COOH gives signals at different positions, why? **10**

(d) Why does $(Ph)_3C-C(Ph)_3$ produce colour when dissolved in any polar solvent? **10**

(e) Write suitable reagents for converting cyclohexene to $OHC(CH_2)_4CHO$. **10**

8. (a) When does p-cresol not produce thermosetting polymer with $H_2C=O$ (drawn as H, H>C=O)? Explain. **15**

(b) What is the name of the reaction

[Figure: (Z)-$CH_3-CH=CH-CH=CD_2$ (s-cis diene drawn with CH_3 and $=CD_2$ ends facing each other) → $CH_2=CH-CH=CH-CHD_2$ (same s-cis shape, ends $=CH_2$ and CHD_2)] **5**

(c) What are the structural differences between Nylon 6.6 and Nylon 6? **10**

(d) How are the following compounds distinguished by mass spectrometry? (A) $DCH_2CH_2COCH_3$ (B) $CH_3CH_2COCH_2D$ (C) $CH_3CHDCOCH_3$ **15**

(e) Write the reactions which produce vinyl chloride from ethanol (in three steps). **15**

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