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Organic Compounds Containing Halogens — JEE (Main) Pattern Topic Test

FREE SAMPLE TEST · CHEMISTRY · PATTERN OF JEE (MAIN)

DURATION	MAXIMUM MARKS	QUESTIONS	NAME / ROLL NO.
60 minutes	100	25 (20 + 5)	

GENERAL INSTRUCTIONS

1. This question paper has two sections, A and B. All 25 questions are compulsory.
2. Section A has TWENTY (20) multiple-choice questions. Each has FOUR options, (1), (2), (3) and (4), of which ONLY ONE is correct.
3. Section B has FIVE (05) questions whose answer is a numerical value. Enter the value rounded off to the nearest integer.
4. Marking scheme for both sections: +4 for a correct answer, −1 for an incorrect answer, 0 if the question is not attempted.
5. Use of a calculator, log tables or any other aid is not allowed.
6. The answer key and worked solutions are at the end of this booklet. Attempt the paper in 60 minutes before you look at them.

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Topics covered: Nature of the C–X bond · Physical properties · Preparation of haloalkanes and haloarenes · Classification of halides · SN1 and SN2 reactions · Stereochemistry of substitution · Elimination reactions · Reactions of haloarenes · Polyhalogen compounds

SECTION A (Q1–20) · Multiple choice · +4 / 0 / −1

Each question has FOUR options. ONLY ONE of them is correct.

1. The correct order of the dipole moments of the halomethanes is

(1) $CH_3F > CH_3Cl > CH_3Br > CH_3I$

(2) $CH_3Cl > CH_3F > CH_3Br > CH_3I$

(3) $CH_3I > CH_3Br > CH_3Cl > CH_3F$

(4) $CH_3F > CH_3Br > CH_3Cl > CH_3I$

2. The correct order of the densities of the following liquids at 293 K is

(1) $CCl_4 < CHCl_3 < CH_2Cl_2$

(2) $CHCl_3 < CH_2Cl_2 < CCl_4$

(3) $CH_2Cl_2 < CCl_4 < CHCl_3$

(4) $CH_2Cl_2 < CHCl_3 < CCl_4$

3. Benzenediazonium chloride is converted into iodobenzene by

(1) CuI and HI (Sandmeyer conditions)

(2) Cu powder and HI (Gattermann conditions)

(3) warming with aqueous KI

(4) I_2 in the presence of FeI_3

4. Iodoalkanes are prepared by heating an alcohol with KI and 95% orthophosphoric acid rather than with KI and concentrated sulphuric acid, because

(1) concentrated H_2SO_4 oxidises the HI formed to I_2

(2) H_3PO_4 is a stronger acid than H_2SO_4

(3) H_2SO_4 converts the alcohol into an alkene only

(4) KI does not dissolve in H_2SO_4

5. The correct order of reactivity of the following bromides towards an SN2 reaction with I^- in acetone is

(1) $(CH_3)_3CCH_2Br > (CH_3)_2CHCH_2Br > CH_3CH_2CH_2CH_2Br$

(2) $(CH_3)_2CHCH_2Br > CH_3CH_2CH_2CH_2Br > (CH_3)_3CCH_2Br$

(3) $CH_3CH_2CH_2CH_2Br > (CH_3)_2CHCH_2Br > (CH_3)_3CCH_2Br$

(4) all three react at the same rate because all are primary

6. The correct order of reactivity towards SN1 hydrolysis is

(1) $(C_6H_5)_3CCl > (C_6H_5)_2CHCl > C_6H_5CH_2Cl > CH_3CH_2CH_2Cl$

(2) $C_6H_5CH_2Cl > (C_6H_5)_2CHCl > (C_6H_5)_3CCl > CH_3CH_2CH_2Cl$

(3) $CH_3CH_2CH_2Cl > C_6H_5CH_2Cl > (C_6H_5)_2CHCl > (C_6H_5)_3CCl$

(4) $(C_6H_5)_2CHCl > (C_6H_5)_3CCl > C_6H_5CH_2Cl > CH_3CH_2CH_2Cl$

7. (R)-2-Bromobutane is heated with sodium cyanide in DMSO, and the reaction goes entirely by the SN2 mechanism. The product is

(1) (R)-2-methylbutanenitrile

(2) (S)-2-methylbutanenitrile

(3) a racemic mixture of 2-methylbutanenitrile

(4) (R)-pentanenitrile

8. 3-Chlorobut-1-ene, $CH_2=CH–CH(Cl)–CH_3$, is warmed with water (SN1 conditions). The product is

(1) but-3-en-2-ol only

(2) but-2-en-1-ol only

(3) butan-2-ol

(4) a mixture of but-3-en-2-ol and but-2-en-1-ol

9. 2-Bromo-3-methylbutane is heated with ethanolic KOH. The major product is

(1) 3-methylbut-1-ene

(2) 2-methylbut-2-ene

(3) 2-methylbut-1-ene

(4) 3-methylbutan-2-ol

10. 2-Bromo-2-methylpropane is heated with sodium ethoxide in ethanol. The main organic product is

(1) 2-ethoxy-2-methylpropane

(2) 2-methylpropan-2-ol

(3) 2-methylpropene

(4) 2-methylpropane

11. Bromoethane is heated with potassium nitrite (KNO_2) in ethanol. The main organic product is

(1) nitroethane, $CH_3CH_2–NO_2$

(2) ethyl nitrite, $CH_3CH_2–O–N=O$

(3) ethanol

(4) ethylamine

12. The correct order of reactivity of the following towards nucleophilic substitution by aqueous NaOH is

(1) 1-chloro-2,4-dinitrobenzene > 1-chloro-4-nitrobenzene > 1-chloro-3-nitrobenzene > chlorobenzene

(2) 1-chloro-4-nitrobenzene > 1-chloro-3-nitrobenzene > 1-chloro-2,4-dinitrobenzene > chlorobenzene

(3) chlorobenzene > 1-chloro-3-nitrobenzene > 1-chloro-4-nitrobenzene > 1-chloro-2,4-dinitrobenzene

(4) 1-chloro-2,4-dinitrobenzene > 1-chloro-3-nitrobenzene > 1-chloro-4-nitrobenzene > chlorobenzene

13. A mixture of chlorobenzene and chloromethane is treated with sodium in dry ether. The product formed by joining the two different groups is

(1) biphenyl

(2) ethylbenzene

(3) toluene

(4) benzene

14. Which of the following is a secondary benzylic halide?

(1) $C_6H_5CH_2Cl$

(2) $C_6H_5CH_2CH_2Cl$

(3) 4-chlorotoluene, $CH_3C_6H_4Cl$

(4) $C_6H_5CH(Cl)CH_3$

15. Chloroform is stored in dark coloured bottles filled to the brim because, in air and light, it is slowly oxidised to

(1) CCl_4 and H_2O

(2) CO_2 and Cl_2

(3) $COCl_2$ and HCl

(4) CH_2Cl_2 and Cl_2O

16. Iodoform was once used as an antiseptic. Its antiseptic action is due to

(1) its pleasant smell

(2) the free iodine it releases

(3) its high solubility in water

(4) the HI it forms with water

17. DDT is manufactured by heating chlorobenzene with compound X in the presence of concentrated sulphuric acid; water is the only other product. X is

(1) chloral, CCl_3CHO

(2) chloroform, $CHCl_3$

(3) carbon tetrachloride, CCl_4

(4) trichloroacetic acid, CCl_3COOH

18. Statement I: Freons such as CCl_2F_2 are used as refrigerants because they are stable, unreactive, non-toxic and easily liquefied gases.
Statement II: In the stratosphere, ultraviolet light breaks the C–Cl bond of a freon, and each chlorine radical formed can destroy many ozone molecules in a chain reaction.
In the light of the above statements, choose the correct answer from the options given below:

(1) Both Statement I and Statement II are true

(2) Statement I is true but Statement II is false

(3) Statement I is false but Statement II is true

(4) Both Statement I and Statement II are false

19. Assertion A: Bromomethane reacts with I^- much faster in acetone than in methanol.
Reason R: In methanol the iodide ion is surrounded by solvent molecules hydrogen-bonded to it, which lowers its ability to attack the carbon.
In the light of the above statements, choose the correct answer from the options given below:

(1) Both A and R are true and R is the correct explanation of A

(2) Both A and R are true but R is NOT the correct explanation of A

(3) A is true but R is false

(4) A is false but R is true

20. Which of the following does NOT give a precipitate when warmed with ethanolic silver nitrate?

(1) benzyl chloride, $C_6H_5CH_2Cl$

(2) allyl chloride, $CH_2{=}CHCH_2Cl$

(3) 2-chloropropane

(4) chlorobenzene

SECTION B (Q21–25) · Numerical value · +4 / 0 / −1

The answer to each question is a NUMERICAL VALUE. Enter it rounded off to the nearest integer.

21. The total number of isomers, including stereoisomers, of the monochloro compounds with the molecular formula $C_5H_{11}Cl$ is _____.

Answer: _____

22. Optically pure (S)-2-bromooctane is hydrolysed. 70% of the product is formed with inversion of configuration and the rest as a racemic mixture. The percentage of (R)-octan-2-ol in the product (to the nearest integer) is _____.

Answer: _____

23. The SN2 reaction $CH_3CH_2Br + OH^- \rightarrow CH_3CH_2OH + Br^-$ has a rate of 2.0×10^{-5} mol L^{-1} s^{-1} when $[CH_3CH_2Br]$ = 0.10 M and $[OH^-]$ = 0.20 M. The rate constant is $x \times 10^{-4}$ L mol^{-1} s^{-1}. The value of x is _____.

Answer: _____

24. The mass of DDT (in g, to the nearest integer) obtained from 225 g of chlorobenzene and excess chloral, if the yield is 80%, is _____. (H = 1, C = 12, O = 16, Cl = 35.5)

Answer: _____

25. In the refrigerant numbering code, adding 90 to the code number gives a three-digit number whose digits are the numbers of C, H and F atoms; the remaining valencies are filled by Cl. For example Freon-12: 12 + 90 = 102, i.e. 1 C, 0 H, 2 F: CCl_2F_2. The code number of the refrigerant $C_2HCl_2F_3$ is _____.

Answer: _____

END OF THE QUESTION PAPER

ANSWER KEY

Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8	Q9	Q10
(2)	(4)	(3)	(1)	(3)	(1)	(2)	(4)	(2)	(3)

Q11	Q12	Q13	Q14	Q15	Q16	Q17	Q18	Q19	Q20
(2)	(1)	(3)	(4)	(3)	(2)	(1)	(1)	(1)	(4)

Q21	Q22	Q23	Q24	Q25
11	85	10	284	123

WORKED SOLUTIONS

Q1. Answer (2). Dipole moment = charge separation × bond length. Fluorine is the most electronegative, but the C–F bond is so short that the product is slightly smaller than for C–Cl. Measured values: CH_3Cl 1.860 D > CH_3F 1.847 D > CH_3Br 1.830 D > CH_3I 1.636 D.

Q2. Answer (4). Density rises as more of the heavy chlorine atoms replace hydrogen: CH_2Cl_2 (1.336 g/mL) < $CHCl_3$ (1.489 g/mL) < CCl_4 (1.595 g/mL). All three are denser than water.

Q3. Answer (3). The iodide ion is a strong enough nucleophile (and reducing agent) to replace the diazonium group directly: $C_6H_5N_2^+Cl^- + KI \rightarrow C_6H_5I + KCl + N_2$. No copper catalyst is needed, unlike for the chloro and bromo compounds.

Q4. Answer (1). KI + acid gives HI, which then converts R–OH into R–I. Concentrated H_2SO_4 is an oxidising agent and oxidises HI to I_2 ($2HI + H_2SO_4 \rightarrow I_2 + SO_2 + 2H_2O$), so little HI is left. H_3PO_4 is non-oxidising.

Q5. Answer (3). All three are primary, but branching on the carbon next to C–Br (the β-carbon) crowds the back side, where the nucleophile must attack. Relative rates: 1-bromobutane about 0.4, 1-bromo-2-methylpropane about 0.03, and 1-bromo-2,2-dimethylpropane (neopentyl bromide) about 10^{-5}, compared with bromoethane = 1.

Q6. Answer (1). The rate of SN1 depends on the stability of the carbocation. Each phenyl ring on the cationic carbon spreads the positive charge by resonance, so trityl (three rings) > benzhydryl (two) > benzyl (one) > propyl (a primary cation, no resonance).

Q7. Answer (2). SN2 attack from the back side inverts the configuration. The priorities before (Br > C_2H_5 > CH_3 > H) and after (CN > C_2H_5 > CH_3 > H; the CN carbon carries (N, N, N), the CH_2 carbon (C, H, H)) are in the same order, with the new group in the place of the old one, so the inversion also changes the label: (S)-2-methylbutanenitrile.

Q8. Answer (4). Loss of Cl^- gives an allylic carbocation whose positive charge is shared between C-3 and C-1 by resonance: $CH_2=CH–CH^+–CH_3 \leftrightarrow {}^+CH_2–CH=CH–CH_3$. Water attacks both ends, giving $CH_2=CH–CH(OH)–CH_3$ (but-3-en-2-ol) and $HOCH_2–CH=CH–CH_3$ (but-2-en-1-ol).

Q9. Answer (2). There are two kinds of β-hydrogen: on C-1 (giving $CH_2=CH–CH(CH_3)_2$, 3-methylbut-1-ene, one alkyl group on the C=C) and on C-3 (giving $CH_3–CH=C(CH_3)_2$, 2-methylbut-2-ene, three alkyl groups). By Saytzeff's rule the more substituted alkene is the major product. 2-Methylbut-1-ene cannot form, because its C=C does not include the carbon that carried Br.

Q10. Answer (3). The halide is tertiary, so back-side SN2 attack is blocked, and ethoxide is a strong base. It removes a β-hydrogen (E2): $(CH_3)_3CBr + C_2H_5O^- \rightarrow CH_2=C(CH_3)_2 + C_2H_5OH + Br^-$. The ether (Williamson product) forms only from primary halides.

Q11. Answer (2). The nitrite ion is ambidentate. KNO_2 is ionic, and the free ion attacks mainly through the negatively charged oxygen, giving the alkyl nitrite R–O–N=O. (With covalent $AgNO_2$ attack through the nitrogen lone pair gives the nitroalkane.)

Q12. Answer (1). The nucleophile adds to the ring first, giving a negatively charged intermediate. A nitro group ortho or para to Cl takes this charge on to its oxygens by resonance; a meta nitro group can only help by its −I effect. So two o/p nitro groups > one para nitro > one meta nitro > none.

Q13. Answer (3). Wurtz–Fittig reaction: $C_6H_5Cl + CH_3Cl + 2Na \rightarrow C_6H_5–CH_3 + 2NaCl$. The aryl and alkyl groups join to give toluene (C_7H_8). Joining two aryl groups gives biphenyl and two methyl groups ethane, as side products.

Q14. Answer (4). In a benzylic halide the halogen is on an sp^3 carbon joined to a benzene ring. In $C_6H_5CH(Cl)CH_3$ that carbon is joined to two carbons (the ring and CH_3): secondary benzylic. $C_6H_5CH_2Cl$ is primary benzylic, $C_6H_5CH_2CH_2Cl$ is not benzylic, and 4-chlorotoluene is an aryl halide.

Q15. Answer (3). $2CHCl_3 + O_2 \rightarrow 2COCl_2 + 2HCl$ (light). Carbonyl chloride, $COCl_2$ (phosgene), is extremely poisonous. Keeping out light and air prevents this; a little ethanol is also added, which turns any phosgene into harmless diethyl carbonate.

Q16. Answer (2). Iodoform itself is not the antiseptic; on contact with the skin it slowly gives off free iodine, which acts as the antiseptic. Because of its very unpleasant smell it has been replaced by other iodine preparations.

Q17. Answer (1). $2C_6H_5Cl + CCl_3CHO \rightarrow (ClC_6H_4)_2CH–CCl_3 + H_2O$. The atoms balance only with chloral: C 12 + 2 = 14, H 10 + 1 − 2 = 9, Cl 2 + 3 = 5 and O 1 − 1 = 0, giving $C_{14}H_9Cl_5$ (p,p′-dichlorodiphenyltrichloroethane).

Q18. Answer (1). I is true; these properties made freons ideal for refrigerators and aerosol sprays. II is true: $CF_2Cl_2 \rightarrow {\bullet}CF_2Cl + Cl{\bullet}$; $Cl{\bullet} + O_3 \rightarrow ClO{\bullet} + O_2$; $ClO{\bullet} + O \rightarrow Cl{\bullet} + O_2$, so $Cl{\bullet}$ is regenerated and the chain goes on. This is why freons were phased out.

Q19. Answer (1). SN2 needs a free, reactive nucleophile. Protic solvents such as methanol solvate anions through hydrogen bonds, stabilising them and lowering their nucleophilicity; acetone (polar aprotic) leaves the anion free. Both are true and R explains A.

Q20. Answer (4). $AgNO_3$ removes Cl^- from halides that can lose it (by SN1); benzyl and allyl chlorides do so very easily (resonance-stabilised cations) and 2-chloropropane on warming. In chlorobenzene Cl is on an sp^2 carbon and the C–Cl bond has partial double bond character, so no AgCl forms.

Q21. Answer 11. There are 8 structural isomers: 1-chloropentane, 2-chloropentane*, 3-chloropentane, 1-chloro-2-methylbutane*, 2-chloro-2-methylbutane, 2-chloro-3-methylbutane*, 1-chloro-3-methylbutane and 1-chloro-2,2-dimethylpropane. The three marked * each have one chiral carbon and exist as a pair of enantiomers: 8 + 3 = 11.

Q22. Answer 85. Inversion gives (R)-octan-2-ol (OH takes the priority place of Br, so the label changes): 70%. The racemic 30% is half R and half S: 15% R. Total R = 70 + 15 = 85%.

Q23. Answer 10. Rate = k[RBr][OH^-], so $k = 2.0 \times 10^{-5} / (0.10 \times 0.20) = 1.0 \times 10^{-3}$ L mol^{-1} $s^{-1} = 10 \times 10^{-4}$. x = 10.

Q24. Answer 284. $2C_6H_5Cl + CCl_3CHO \rightarrow C_{14}H_9Cl_5 + H_2O$. Chlorobenzene: 225/112.5 = 2.0 mol, giving 1.0 mol DDT (M = 168 + 9 + 177.5 = 354.5 g/mol) in theory. At 80%: 0.80 × 354.5 = 283.6 g, i.e. 284.

Q25. Answer 123. $C_2HCl_2F_3$ has 2 C, 1 H and 3 F, so the three-digit number is 213, and the code is 213 − 90 = 123 (HCFC-123). Check: 2 C need 6 other atoms: 1 H + 3 F + 2 Cl = 6.

All questions are original and © Master Testing Agency. Free to download and use for personal practice; not for resale. Every answer in this paper was checked independently by computer: structures were built as graphs; isomer counts by placing the halogen on every carbon skeleton, chiral centres, elimination and allylic products and R/S labels after inversion were worked out on the graphs, equations and masses from atom counts, and the data questions from tables of measured values.