SOLVED PAPER · ANSWER KEY WITH EXPLANATIONS

UPSC Combined Geo-Scientist (Prelims) 2020

Paper II: Chemistry · 120 questions · 300 marks · 2 hours

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How to use this sheet. Attempt the paper first (it is free to read and download on vkcscience.com). Then check your answers with the key below and read the explanation of every question you got wrong or guessed. Key words are in **blue**. Numericals show formula, substitution and result.

Answer key

1 **c**	2 **b**	3 **c**	4 **b**	5 **c**	6 **b**	7 **c**	8 **a**	9 **c**	10 **c**	11 **d**	12 **a**
13 **a**	14 **d**	15 **b**	16 **d**	17 **d**	18 **c**	19 **c**	20 **a**	21 **d**	22 **a**	23 **a**	24 **b**
25 **c**	26 **d**	27 **b**	28 **b**	29 **b**	30 **b**	31 **d**	32 **c**	33 **b**	34 **b**	35 **c**	36 **c**
37 **b**	38 **b**	39 **a**	40 **c**	41 **a**	42 **a**	43 **a**	44 **d**	45 **c**	46 **c**	47 **a**	48 **b**
49 **b**	50 **a**	51 **b**	52 **a**	53 **d**	54 **c**	55 **b**	56 **b**	57 **d**	58 **c**	59 **d**	60 **a**
61 **b**	62 **d**	63 **c**	64 **a**	65 **d**	66 **c**	67 **c**	68 **c**	69 **a**	70 **d**	71 **b**	72 **d**
73 **a**	74 **b**	75 **a**	76 **b**	77 **b**	78 **a**	79 **b**	80 **a**	81 **d**	82 **c**	83 **b**	84 **b**
85 **b**	86 **d**	87 **c**	88 **d**	89 **b**	90 **b**	91 **d**	92 **b**	93 **a**	94 **c**	95 **a**	96 **a**
97 **c**	98 **b**	99 **a**	100 **a**	101 **c**	102 **c**	103 **c**	104 **a**	105 **d**	106 **c**	107 **b**	108 **c**
109 **c**	110 **a**	111 **d**	112 **a**	113 **c**	114 **d**	115 **d**	116 **d**	117 **c**	118 **a**	119 **c**	120 **b**

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Q1 Atomic structure / wave functions

Consider the following statements regarding radial and total angular function of H-atom:

1. The radial function R(r) depends on the quantum number n and l
2. The total angular function depends only on the direction and is independent of the distance from the nucleus (r)

Which of the statements given above is/are correct?

(a) 1 only
(b) 2 only
(c) Both 1 and 2
(d) Neither 1 nor 2

Answer: (c) Both 1 and 2

$\psi = R(r)\cdot Y(\theta,\varphi)$. 1 ✔ The **radial part R(r)** depends on **n and l** (e.g. $R_{20} \neq R_{21}$). 2 ✔ The **angular part Y(θ,φ)** depends only on **direction** (l, m), not on r. Both correct → (c). Remember: radial nodes = n − l − 1; angular nodes = l.

Q2 Atomic structure / configuration

Which one of the following is the correct electronic configuration of gold (ground state)?

(a) [Xe] $6s^2\ 4f^{14}\ 5d^9$
(b) [Xe] $6s^1\ 4f^{14}\ 5d^{10}$
(c) [Xe] $6s^2\ 4f^{13}\ 5d^{10}$
(d) [Xe] $6s^2\ 4f^{14}\ 5d^{10}$

Answer: (b) [Xe] $6s^1\ 4f^{14}\ 5d^{10}$

Au (Z = 79) is like Cu and Ag: a **full d^{10}** is more stable, so one 6s electron moves to 5d. Ground state: **[Xe] $4f^{14}\ 5d^{10}\ 6s^1$** → (b). Relativistic contraction of 6s in Au supports this.

Q3 Periodic properties / oxides

Which one of the following is the correct order of increasing acidic nature of oxides?

(a) $SiO_2 < Al_2O_3 < SO_3 < Cl_2O_7$
(b) $SiO_2 < SO_3 < Al_2O_3 < Cl_2O_7$
(c) $Al_2O_3 < SiO_2 < SO_3 < Cl_2O_7$
(d) $Cl_2O_7 < SiO_2 < SO_3 < Al_2O_3$

Answer: (c) $Al_2O_3 < SiO_2 < SO_3 < Cl_2O_7$

Across period 3, oxides go from basic → **amphoteric** → acidic as the oxidation state and electronegativity of the element rise: **Al_2O_3 (amphoteric) < SiO_2 (weakly acidic) < SO_3 < Cl_2O_7** (strongest, gives $HClO_4$) → (c).

Q4 Periodic table / blocks

Which one of the following is the correct outermost electronic configuration of representative elements?

(a) $(n-1)d^{1-10}\ ns^{0-2}$
(b) ns^{1-2} to ns^2np^{1-6}
(c) $(n-2)f^{1-14}\ (n-1)d^{0-1}\ ns^2$
(d) ns^0

Answer: (b) ns^{1-2} to ns^2np^{1-6}

Representative (main-group) elements = s- and p-block: outer configuration **ns^{1-2}** (s-block) to **$ns^2\ np^{1-6}$** (p-block) → (b). (a) is d-block, (c) f-block.

Q5 Periodic table / new elements

The name of the element given by IUPAC with atomic number 118 is:

(a) Nihonium
(b) Moscovium
(c) Oganesson
(d) Tennessine

Answer: (c) Oganesson

IUPAC names (2016): 113 **Nihonium**, 115 **Moscovium**, 117 **Tennessine**, 118 **Oganesson** (Og, after Yuri Oganessian) → (c).

Q6 f-block / actinoids

Which one of the following statements regarding actinoid metals is NOT correct?

(a) The actinoid metals are usually silvery in appearance
(b) Ionization enthalpies of the early actinoids are higher than that of the early lanthanoids
(c) The actinoids are highly reactive metals
(d) The actinoid metals in general show +3 oxidation state

Answer: (b) Ionization enthalpies of the early actinoids are higher than that of the early lanthanoids

(a) ✔ silvery metals. (c) ✔ highly reactive, esp. finely divided. (d) ✔ +3 is common. (b) ✘ 5f electrons are **less shielded by** inner core and **less penetrating** than 4f, so early actinoids have **lower** ionisation enthalpies than early lanthanoids → (b) is NOT correct.

Q7 Periodic properties / ionic radius

Which one of the following is the correct order of ionic radius?

(a) $F^- > O^{2-} > Na^+$
(b) $Na^+ > F^- > O^{2-}$
(c) $H^- > H > H^+$
(d) $Al^{3+} > Mg^{2+} > N^{3-}$

Answer: (c) $H^- > H > H^+$

Isoelectronic: more negative charge → larger. $O^{2-} > F^- > Na^+$, and $N^{3-} > Mg^{2+} > Al^{3+}$, so (a), (b), (d) are reversed. **H^- ($1s^2$) > H ($1s^1$) > H^+** (bare proton) → (c). Remember: adding electrons expands the cloud; removing shrinks it.

Q8 Periodic properties / ionisation energy

Which one among the following elements has the highest second ionization potential?

(a) B
(b) Be
(c) Mg
(d) Al

Answer: (a) B

IE_2 removes an electron from the **cation**. $B^+ = 1s^2\ 2s^2$ (stable filled 2s, small size) → **$IE_2 \approx 25.2$ eV**. Be^+ ($2s^1$) ≈ 18.2, Al^+ ($3s^2$) ≈ 18.8, Mg^+ ($3s^1$) ≈ 15.0 eV → B highest → (a).

Q9 Coordination / magnetism (VBT/CFT)

Consider the following statements regarding magnetism of two complexes:

CoF_6^{3-} is a paramagnetic and high spin complex
$Co(NH_3)_6^{3+}$ is a diamagnetic and low spin complex

Which of the statements given above is/are correct?

(a) 1 only
(b) 2 only
(c) Both 1 and 2
(d) Neither 1 nor 2

Answer: (c) Both 1 and 2

$Co^{3+} = d^6$. 1 ✔ **F^- weak field** → high spin $t_2g^4eg^2$, **4 unpaired**, paramagnetic (sp^3d^2, outer orbital). 2 ✔ **NH_3 strong** for Co^{3+} → low spin t_2g^6, **diamagnetic** (d^2sp^3). Both → (c).

Q10 s-block / solubility

Consider the following statements in respect of alkali metal halides:

1. The low solubility of LiF in water is due to its high lattice enthalpy
2. The low solubility of CsI in water is due to smaller hydration enthalpy of its two ions

Which of the statements given above is/are correct?

(a) 1 only
(b) 2 only
(c) Both 1 and 2
(d) Neither 1 nor 2

Answer: (c) Both 1 and 2

Solubility depends on **lattice enthalpy vs hydration enthalpy**. 1 ✔ LiF: tiny Li^+ and F^- → very **high lattice enthalpy** → poorly soluble. 2 ✔ CsI: both ions large → **low hydration enthalpy** → poorly soluble. Both → (c).

Q11 Solid state / radius ratio

When the radius ratio in an ionic crystal lies between 0.732 – 0.999, the coordination number will be:

(a) 3 (b) 4
(c) 6 (d) 8

Answer: (d) 8

r^+/r^- limits: 0.155–0.225 → CN 3; 0.225–0.414 → 4; 0.414–0.732 → 6; **0.732–1.0 → CN 8** (cubic, e.g. **CsCl**) → (d).

Q12 s-block / thermal stability

Which one of the following is the correct order of thermal stabilities of metal carbonates?

(a) $BaCO_3 > CaCO_3 > MgCO_3 > BeCO_3$ (b) $BaCO_3 > MgCO_3 > CaCO_3 > BeCO_3$
(c) $CaCO_3 > BaCO_3 > MgCO_3 > BeCO_3$ (d) $BaCO_3 > BeCO_3 > MgCO_3 > CaCO_3$

Answer: (a) $BaCO_3 > CaCO_3 > MgCO_3 > BeCO_3$

Larger cation → **less polarisation** of CO_3^{2-} → more stable carbonate. Down group 2 stability rises: **$BaCO_3 > SrCO_3 > CaCO_3 > MgCO_3 > BeCO_3$** → (a). $BeCO_3$ is so unstable it is kept under CO_2.

Q13 Bonding / Fajans' rules

Which one of the following is the correct order of increasing covalent character of halides of Al^{3+}?

(a) $AlF_3 < AlCl_3 < AlBr_3 < AlI_3$ (b) $AlI_3 < AlBr_3 < AlCl_3 < AlF_3$
(c) $AlF_3 < AlBr_3 < AlCl_3 < AlI_3$ (d) $AlCl_3 < AlF_3 < AlBr_3 < AlI_3$

Answer: (a) $AlF_3 < AlCl_3 < AlBr_3 < AlI_3$

Same cation Al^{3+}; **larger, softer anion is more polarisable** → more covalent. $F^- < Cl^- < Br^- < I^-$ in size, so covalent character **$AlF_3 < AlCl_3 < AlBr_3 < AlI_3$** → (a). AlF_3 is ionic (m.p. ~1290 °C); $AlCl_3$ sublimes.

Q14 Solid state / defects

The appearance of colour in solid alkali metal halides is generally due to:

(a) Schottky defect (b) Frenkel defect
(c) Interstitial Position (d) F-Centres

Answer: (d) F-Centres

Heating alkali halides in alkali vapour gives **metal-excess defect**: anion vacancies trap electrons = **F-centres** (Farbenzentren). They absorb visible light: NaCl yellow, KCl violet, LiCl pink → (d).

Q15 VSEPR / shapes

Match List-I with List-II and select the correct answer using the code given below the lists:

List-I (Molecule/ion)	**List-II (Shape)**
A. H_2O	1. Linear
B. BF_3	2. Angular
C. I_3^-	3. Trigonal planar
D. SF_4	4. See-saw

Code:

(a) A-4, B-1, C-3, D-2 (b) A-2, B-3, C-1, D-4
(c) A-2, B-1, C-3, D-4 (d) A-4, B-3, C-1, D-2

Answer: (b) A-2, B-3, C-1, D-4

A. H_2O: 2 bp + 2 lp → **angular** (2). B. BF_3: 3 bp → **trigonal planar** (3). C. I_3^-: 2 bp + 3 lp → **linear** (1). D. SF_4: 4 bp + 1 lp → **see-saw** (4). Code 2-3-1-4 → (b).

Q16 VSEPR / bond lengths

In which of the following molecules/ions, all the bond lengths are NOT equal?

(a) BF_3
(b) BF_4^-
(c) XeF_4
(d) SF_4

Answer: (d) SF_4

BF_3 (trigonal planar), BF_4^- (tetrahedral), XeF_4 (square planar) have all bonds equivalent. **SF_4** is **see-saw** (sp^3d): 2 **axial** S–F (164.6 pm) are longer than 2 **equatorial** (154.5 pm) → (d).

Q17 MO theory / bond order

Which one of the following exhibits highest bond order?

(a) O_2
(b) O_2^-
(c) O_2^{2-}
(d) O_2^+

Answer: (d) O_2^+

BO = (Nb – Na)/2. O_2^+ (15 e^-) **2.5**; O_2 2.0; O_2^- 1.5; O_2^{2-} 1.0. Highest = **O_2^+** → (d). Trick: removing an antibonding π* electron raises BO.

Q18 Bonding / resonance

How many resonating structures are possible for NO_3^- ion?

(a) 4
(b) 5
(c) 6
(d) 3

Answer: (c) 6

NO_3^- (24 valence e^-): N forms one N=O and two N–O^-. The **double bond can sit on any of the 3 O atoms** → **3 equivalent major contributors**, each N–O bond order 4/3. UPSC's key counts **6**, i.e. it also counts the minor charge-separated forms → (c).

Q19 Coordination / VBT

Consider the following statements for the complex $[Ni(NH_3)_6]Cl_2$:

1. It is an outer orbital octahedral complex
2. Hybridization of Ni is sp^3d^2
3. It is a paramagnetic complex
4. It is a diamagnetic complex

Which of the statements given above are correct?

(a) 1 and 2 only
(b) 2 and 3 only
(c) 1, 2 and 3
(d) 1, 2 and 4

Answer: (c) 1, 2 and 3

Ni^{2+} = $3d^8$. Octahedral with NH_3: inner 3d has no two empty orbitals, so **sp^3d^2** (outer 4d) → **outer-orbital** complex. 2 unpaired e^- → **paramagnetic** (μ ≈ 2.83 BM). 1 ✔ 2 ✔ 3 ✔ 4 ✘ → (c).

Q20 Qualitative analysis / sulfide test

Sodium nitroprusside when added to an alkaline solution of sulphide ion gives red coloured solution. The red colouration is due to the formation of:

(a) $Na_4[Fe(CN)_5(NOS)]$
(b) $Na_2[Fe(CN)_5(NO)]$
(c) $Na_4[FeCl_5(NOS)]$
(d) $[Fe(H_2O)_5(NO)]SO_4$

Answer: (a) $Na_4[Fe(CN)_5(NOS)]$

Sodium nitroprusside $Na_2[Fe(CN)_5NO]$ + S^{2-} (alkaline) → **$Na_4[Fe(CN)_5NOS]$**, a **violet/purple-red** complex. S^{2-} adds to the NO ligand → (a). Remember: same test is used for S in Lassaigne's extract.

Q21 Coordination / geometry and magnetism

The complex ions $[NiCl_4]^{2-}$ and $[Ni(CN)_4]^{2-}$ are:

(a) Both square planar
(b) Both diamagnetic
(c) Both paramagnetic
(d) Paramagnetic and diamagnetic respectively

Answer: (d) Paramagnetic and diamagnetic respectively

$[NiCl_4]^{2-}$: Cl^- weak, **sp^3 tetrahedral**, 2 unpaired e^- → **paramagnetic**. $[Ni(CN)_4]^{2-}$: CN^- strong, pairs electrons, **dsp^2 square planar** → **diamagnetic** → (d).

Q22 Coordination / unpaired electrons

Consider the following complexes:

$Fe(H_2O)_6^{2+}$
$Fe(CN)_6^{3-}$
$Fe(CN)_6^{4-}$
$Fe(H_2O)_6^{3+}$

Which one of the following is the correct order of number of unpaired electrons in the above complexes?

(a) 4 > 1 > 2 > 3
(b) 1 > 2 > 3 > 4
(c) 3 > 2 > 1 > 4
(d) 4 > 2 > 1 > 3

Answer: (a) 4 > 1 > 2 > 3

4. $[Fe(H_2O)_6]^{3+}$ d^5 high spin → **5**. 1. $[Fe(H_2O)_6]^{2+}$ d^6 high spin → **4**. 2. $[Fe(CN)_6]^{3-}$ d^5 low spin → **1**. 3. $[Fe(CN)_6]^{4-}$ d^6 low spin → **0**. Order 4 > 1 > 2 > 3 → (a).

Q23 Coordination / denticity

The denticity of ligands glycinate, iminodiacetic acid and nitrilotriacetic acid are:

(a) 2, 3 and 4 respectively
(b) 3, 3 and 4 respectively
(c) 2, 3 and 3 respectively
(d) 1, 2 and 3 respectively

Answer: (a) 2, 3 and 4 respectively

Glycinate $NH_2CH_2COO^-$ binds via N and O → **2**. **Iminodiacetate** $HN(CH_2COO^-)_2$: N + 2 O → **3**. **Nitrilotriacetate** $N(CH_2COO^-)_3$: N + 3 O → **4** → (a).

Q24 Coordination / nomenclature

Which one of the following is the IUPAC name of the complex $K_3[Fe(CN)_6]$?

(a) Potassium hexacyanoferrate(II)
(b) Potassium hexacyanoferrate(III)
(c) Trispotassium hexacyanoiron(III)
(d) Potassium hexacyanoiron(III)

Answer: (b) Potassium hexacyanoferrate(III)

$K_3[Fe(CN)_6]$: anion charge −3; 6 CN^- = −6 → **Fe = +3**. Anionic complex → metal ends in **-ate**, iron → **ferrate**. Name: **potassium hexacyanoferrate(III)** → (b). (Ferrate(II) is $K_4[Fe(CN)_6]$.)

Q25 Coordination / geometrical isomerism

Which one of the following complexes will NOT show geometrical isomerism?

(a) $[Cr(NH_3)_4Cl_2]Cl$
(b) $[Co(en)_2Cl_2]Cl$
(c) $[Co(NH_3)_5NO_2]Cl_2$
(d) $Pt(NH_3)_2Cl_2$

Answer: (c) $[Co(NH_3)_5NO_2]Cl_2$

MA_4B_2 ($[Cr(NH_3)_4Cl_2]^+$), $M(AA)_2B_2$ ($[Co(en)_2Cl_2]^+$) and square planar MA_2B_2 ($Pt(NH_3)_2Cl_2$) all show **cis/trans**. **$[Co(NH_3)_5NO_2]^{2+}$ is MA_5B**: only one arrangement → no geometrical isomers → (c). (It shows linkage isomerism.)

Q26 Coordination / optical isomerism

Which one of the following complexes exhibits optical isomerism?

(a) cis-$[PtCl_2(NH_3)_2]$ (b) trans-$[PtCl_2(NH_3)_2]$
(c) trans-$[Co(en)_2Cl_2]^+$ (d) $[Co(EDTA)]^-$

Answer: (d) $[Co(EDTA)]^-$

Square planar Pt complexes have a **mirror plane** → optically inactive. trans-$[Co(en)_2Cl_2]^+$ has a plane of symmetry. **$[Co(EDTA)]^-$**: hexadentate ligand wraps the metal in a **chiral** arrangement (like $M(AA)_3$) → optically active → (d).

Q27 Coordination / optical activity

Consider the following complex ions:

$Co(en)_3^{3+}$

1. cis-$[Co(en)_2Cl_2]^+$
2. trans-$[Co(en)_2Cl_2]^+$

Which of the complex ion(s) given above show(s) optical activity?

(a) 1 only (b) 1 and 2
(c) 1 and 3 (d) 2 and 3

Answer: (b) 1 and 2

1 ✔ $[Co(en)_3]^{3+}$ ($M(AA)_3$) has Δ and Λ forms. 2 ✔ **cis**-$[Co(en)_2Cl_2]^+$ is chiral. 3 ✘ **trans** has a mirror plane through Cl–Co–Cl. → 1 and 2 → (b).

Q28 Ionic equilibrium / buffer

A solution is obtained by mixing 10 ml of 0.2 N KOH solution with 30 ml of 0.1 N CH_3COOH. The pH of the solution would be: (Given: pKa of CH_3COOH = 4.75; log 2 = 0.30)

(a) 5.301 (b) 5.05
(c) 4.699 (d) 4.398

Answer: (b) 5.05

KOH = 10 × 0.2 = **2 meq**; CH_3COOH = 30 × 0.1 = **3 meq**. After reaction: salt 2, acid 1 → buffer. pH = pKa + log(salt/acid) = 4.75 + log 2 = 4.75 + 0.30 = **5.05** → (b).

Q29 Ionic equilibrium / buffer

What will be the hydrogen ion concentration of a solution obtained by mixing 500 ml of 0.20 M acetic acid and 500 ml of 0.30 M sodium acetate? (Dissociation constant of acetic acid = 1.75×10^{-5})

(a) 2.75×10^{-5} mol.dm^{-3} (b) 1.17×10^{-5} mol.dm^{-3}
(c) 3.50×10^{-5} mol.dm^{-3} (d) 1.75×10^{-3} mol.dm^{-3}

Answer: (b) 1.17×10^{-5} mol.dm^{-3}

After mixing (1 L total): [HA] = 0.10 M, [A^-] = 0.15 M. **$[H^+] = Ka \cdot [HA]/[A^-]$** = $1.75 \times 10^{-5} \times 0.10/0.15$ = **1.17×10^{-5} mol dm^{-3}** → (b).

Q30 Ionic equilibrium / hydrated cations

Which one of the following represents the correct order of acid strength?

$Fe(H_2O)_6^{2+} < [Al(H_2O)_6]^{3+} < [Fe(H_2O)_6]^{3+}$
$Fe(H_2O)_6^{2+} < [Fe(H_2O)_6]^{3+} < [Al(H_2O)_6]^{3+}$
$Fe(H_2O)_6^{3+} < [Fe(H_2O)_6]^{2+} < [Al(H_2O)_6]^{3+}$
$Fe(H_2O)_6^{3+} < [Al(H_2O)_6]^{3+} < [Fe(H_2O)_6]^{2+}$

Answer: (b) $[Fe(H_2O)_6]^{2+} < [Fe(H_2O)_6]^{3+} < [Al(H_2O)_6]^{3+}$

Acidity of $[M(H_2O)_6]^{n+}$ rises with **charge density** of M^{n+}: Fe^{2+} is weakest. On simple **charge/size** (Al^{3+} 53.5 pm < Fe^{3+} 64.5 pm) the key ranks **$Fe^{2+} < Fe^{3+} < Al^{3+}$** → (b). Note: measured pKa values (Fe^{3+} ≈ 2.2, Al^{3+} ≈ 5.0) actually make Fe^{3+} the

stronger acid, i.e. order (a).

Q31 s-block / hydroxides

Consider the following hydroxides:

1. $Be(OH)_2$
2. $Sr(OH)_2$
3. $Mg(OH)_2$
4. $Ba(OH)_2$

The correct order of basicity of the above hydroxides will be:

(a) $Sr(OH)_2 < Be(OH)_2 < Ba(OH)_2 < Mg(OH)_2$
(b) $Be(OH)_2 < Mg(OH)_2 < Ba(OH)_2 < Sr(OH)_2$
(c) $Mg(OH)_2 < Ba(OH)_2 < Sr(OH)_2 < Be(OH)_2$
(d) $Be(OH)_2 < Mg(OH)_2 < Sr(OH)_2 < Ba(OH)_2$

Answer: (d) $Be(OH)_2 < Mg(OH)_2 < Sr(OH)_2 < Ba(OH)_2$

Down group 2, **ionisation energy falls** and M–OH bond becomes more ionic → **basicity rises**: **$Be(OH)_2$ (amphoteric) < $Mg(OH)_2$ < $Sr(OH)_2$ < $Ba(OH)_2$** → (d). Solubility also rises down the group.

Q32 Acids and bases / Lewis acidity

Which one of the following is the correct order of Lewis Acidity in Boron halides?

(a) $BF_3 < BI_3 < BBr_3 < BCl_3$
(b) $BI_3 < BF_3 < BCl_3 < BBr_3$
(c) $BF_3 < BCl_3 < BBr_3 < BI_3$
(d) $BBr_3 < BI_3 < BF_3 < BCl_3$

Answer: (c) $BF_3 < BCl_3 < BBr_3 < BI_3$

Expected from electronegativity: BF_3 strongest, but actual order is **$BF_3 < BCl_3 < BBr_3 < BI_3$** → (c). Reason: strong **pπ–pπ back-bonding** from F to empty B 2p is lost when BF_3 becomes pyramidal on accepting a lone pair; overlap weakens with larger halogens.

Q33 Ionic equilibrium / pH

Which one of the following statements regarding acid-base property is NOT correct?

(a) pH + pOH = 14, for all aqueous solutions
(b) The pH of 10^{-8} (M) HCl solution is 8
(c) The conjugate base of $H_2PO_4^-$ is HPO_4^{2-}
(d) H_2SO_4 is a strong acid in aqueous solution

Answer: (b) The pH of 10^{-8} (M) HCl solution is 8

(b) ✘ 10^{-8} M HCl cannot be basic: water's own H^+ (10^{-7}) dominates; $[H^+] \approx 1.05 \times 10^{-7}$ → **pH ≈ 6.98**. (c) ✔ $H_2PO_4^-$ − H^+ → HPO_4^{2-}. (d) ✔. (a) holds at 25 °C. NOT correct → (b).

Q34 Ionic equilibrium / pH

What will be the value of pOH of 0.03M aqueous solution of HCl at 25°C? (Given log 0.03 = −1.52)

(a) 12.21
(b) 12.48
(c) 11.48
(d) 10.48

Answer: (b) 12.48

Strong acid: $[H^+]$ = 0.03 M. pH = −log 0.03 = **1.52**. **pOH = 14 − 1.52 = 12.48** → (b).

Q35 Solutions / concentration terms

What will be the value of mole fraction of the solute in 1.00 molal aqueous solution?

(a) 1.7700
(b) 1.7770
(c) 0.0180
(d) 0.0344

Answer: (c) 0.0180

1 molal = 1 mol solute in 1000 g water (1000/18 = **55.5 mol**). x(solute) = 1/(1 + 55.5) = **0.0177 ≈ 0.018** → (c). Trick: mole fraction must be < 1, so (a) and (b) are out at once.

Q36 Redox / equivalent weight

Equivalent weight of $K_2Cr_2O_7$ in acidic medium will be: (Atomic weight of K = 39, Cr = 52 and O = 16)

(a) 294 / 2
(b) 294/ 3
(c) 294/ 6
(d) 294

Answer: (c) 294/ 6

Acidic: $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$ (Cr +6 → +3, two Cr). n-factor = **6**. Eq. wt = M/6 = **294/6** = 49 → (c).

Q37 Volumetric analysis / standards

Which one of the following is a primary standard substance?

(a) $KMnO_4$
(b) $K_2Cr_2O_7$
(c) $Na_2S_2O_3$
(d) NaOH

Answer: (b) $K_2Cr_2O_7$

A **primary standard** must be pure, stable, non-hygroscopic, of known formula and high molar mass. **$K_2Cr_2O_7$** fits → (b). $KMnO_4$ (decomposes, MnO_2 impurity), $Na_2S_2O_3$ (efflorescent, bacterial decay), NaOH (hygroscopic, absorbs CO_2) are secondary standards.

Q38 Volumetric analysis / permanganometry

The equivalence point of titration of oxalate solution (acidic medium) with $KMnO_4$ solution will be:

(a) Pink
(b) Colourless
(c) Orange
(d) Light green

Answer: (b) Colourless

At the **equivalence point** all MnO_4^- added has just been reduced to **Mn^{2+}** (nearly colourless) and all oxalate is used up → solution is **colourless** → (b). The **end point** is one drop later, when excess MnO_4^- gives a permanent **light pink**. Trap: equivalence point ≠ end point.

Q39 Volumetric analysis / indicators

In which of the following titrations, an external indicator is NOT necessary?

(a) Titration of oxalate solution with $KMnO_4$ solution
(b) Titration of HCl with NaOH solution
(c) Titration of Hard water with EDTA
(d) Titration of Na_2CO_3 with HCl solution

Answer: (a) Titration of oxalate solution with $KMnO_4$ solution

Oxalate–$KMnO_4$: **$KMnO_4$ acts as its own indicator** (pink at end point) → no added indicator needed → (a). HCl–NaOH and Na_2CO_3–HCl need acid-base indicators; EDTA–hard water needs Eriochrome Black T.

Q40 Volumetric analysis / complexometry

Which one among the following is a metal ion type indicator?

(a) Methylene blue
(b) Diphenylamine sulphonic acid
(c) Eriochrome black T
(d) Cresol red

Answer: (c) Eriochrome black T

Eriochrome Black T is a **metal-ion (metallochromic) indicator** for EDTA titrations: wine-red Mg–EBT complex → blue free dye at end point (pH 10) → (c). Methylene blue and diphenylamine sulfonic acid are redox indicators; cresol red is an acid-base indicator.

Q41 Gaseous state / kinetic energy

At what temperature does the total kinetic energy of 0.3 mole of Helium equals the total kinetic energy of 0.4 mole of Argon at 400 K?

(a) 533.3 K
(b) 433.3 K
(c) 346.3 K
(d) 373.0 K

Answer: (a) 533.3 K

Total KE = **(3/2) nRT** (independent of M). 0.3 × T = 0.4 × 400 → **T = 533.3 K** → (a).

Q42 Real gases / van der Waals

The ratio of Boyle's temperature (TB) and critical temperature (TC) of a gas obeying van der Waals equation is given by:

(a) TB : TC = 27: 8
(b) TB : TC = 4: 27
(c) TB : TC = 3: 2
(d) TB : TC = 8: 27

Answer: (a) TB : TC = 27: 8

TB = a/(Rb); **TC = 8a/(27Rb)**. TB/TC = 27/8 → **27 : 8** → (a). Remember: Ti (inversion) = 2a/(Rb) = 2TB.

Q43 Real gases / compressibility factor

Weight of O_2 necessary to fill up a cylinder of 0.082 litre capacity at 0°C and 96 atm pressure would be: (Compressibility factor = 0.96 and gas constant (R) = 0.082 dm^3 atm K^{-1} mol^{-1})

(a) 11.72 g
(b) 1.172 g
(c) 117.2 g
(d) 10.72 g

Answer: (a) 11.72 g

PV = ZnRT → n = PV/(ZRT) = (96 × 0.082)/(0.96 × 0.082 × 273) = **0.3663 mol**. Mass = 0.3663 × 32 = **11.72 g** → (a).

Q44 Gaseous state / molecular speed

Which one of the following gas samples will have the highest average molecular speed? (Atomic weight of O = 16, Ne = 20, C = 12 and He = 4)

(a) 1.0 mole of O_2 at 560 K
(b) 0.50 mole of Ne at 500 K
(c) 0.20 mole of CO_2 at 440 K
(d) 2.0 mole of He at 140 K

Answer: (d) 2.0 mole of He at 140 K

Mean speed ∝ **√(T/M)**; amount of gas does not matter. O_2 √(560/32) = 4.18; Ne √(500/20) = 5.00; CO_2 √(440/44) = 3.16; **He √(140/4) = 5.92** → highest → (d).

Q45 Kinetic theory / rms speed

The root mean square velocity of a monoatomic gas of molar mass 'M' (g mol^{-1}) is 'u'. What is the correct relation between 'u' and average kinetic energy (E) per mole?

(a) $u = \sqrt{\frac{3E}{M}}$
(b) $u = \sqrt{\frac{2E}{3M}}$
(c) $u = \sqrt{\frac{2E}{M}}$
(d) $u = \sqrt{\frac{E}{3M}}$

Answer: (c) $u = \sqrt{\frac{2E}{M}}$

Per mole, average KE **E = ½ M u²** (u = rms speed, M = molar mass). So **u = √(2E/M)** → (c). Check: E = (3/2)RT gives u = √(3RT/M), the usual form.

Q46 Thermodynamics / heat capacity

The amount of energy (per mole of a monoatomic gas) that will increase by increasing the temperature by one degree at constant volume is:

(a) Cp – Cv
(b) R/2
(c) 3/2 R
(d) Cv + R

Answer: (c) 3/2 R

Energy to raise 1 mol by 1 K at constant volume = **Cv**. For a **monoatomic** ideal gas, U = (3/2)RT → **Cv = 3/2 R** (≈ 12.5 J K^{-1} mol^{-1}) → (c).

Q47 Kinetic theory / mean free path

Which one among the following gases has the largest mean free path under the same external conditions?

(a) H_2
(b) Cl_2
(c) N_2
(d) O_2

Answer: (a) H_2

$\lambda = kT/(\sqrt{2}\,\pi\, d^2\, P)$. At same T and P, $\lambda \propto$ **$1/d^2$**. **H_2** has the smallest molecular diameter → **largest mean free path** → (a).

Q48 Gaseous state / Graham's law

50 mL of H_2 gas diffuses through a small hole from a vessel in 20 minutes. Time taken by 40 mL of O_2 gas to diffuse under similar condition will be:

(a) 12 minutes
(b) 64 minutes
(c) 8 minutes
(d) 32 minutes

Answer: (b) 64 minutes

Rate $\propto 1/\sqrt{M}$. $r(H_2) = 50/20 = 2.5$ mL/min. $r(O_2) = 2.5 \times \sqrt{(2/32)} =$ **0.625 mL/min**. Time for 40 mL = 40/0.625 = **64 min** → (b).

Q49 Thermodynamics / adiabatic process

What will be the slope of the plot of log P vs log V for a reversible adiabatic expansion of an ideal gas? [γ = Cp/Cv]

(a) γ
(b) $-\gamma$
(c) zero
(d) –1

Answer: (b) $-\gamma$

Reversible adiabatic: **$PV^{\gamma} = constant$** → $\log P = -\gamma \log V + constant$. Slope of log P vs log V = **$-\gamma$** → (b). (Isothermal: slope −1.)

Q50 Thermodynamics / ΔH and ΔU

The latent heat of vaporization of Br_2 at 59°C and at 1 atm pressure is 29.2 kJ mol^{-1}. The value of ΔU would be: ($R = 8.314 \times 10^{-3}$ kJ mol^{-1} K^{-1})

(a) 26.44 kJ mol^{-1}
(b) 2.644 kJ mol^{-1}
(c) 264.4 kJ mol^{-1}
(d) 31.96 kJ mol^{-1}

Answer: (a) 26.44 kJ mol^{-1}

$Br_2(l) \rightarrow Br_2(g)$, $\Delta n(g) = 1$, T = 332 K. **$\Delta U = \Delta H - \Delta nRT$** = $29.2 - 8.314 \times 10^{-3} \times 332 = 29.2 - 2.76 =$ **26.44 kJ mol^{-1}** → (a).

Q51 Thermodynamics / heat capacity ratio

The ratio of specific heat of gases at constant pressure (Cp) and constant volume (Cv) of N_2 molecule is:

(a) 1.667 (b) 1.400
(c) 1.330 (d) 1.520

Answer: (b) 1.400

N_2 is **diatomic**: at room temperature Cv = 5/2 R, Cp = 7/2 R. **γ = 7/5 = 1.40** → (b). Monoatomic 1.67; non-linear polyatomic ~1.33.

Q52 Thermodynamics / enthalpy

The total heat content of a system at constant pressure is known as:

(a) Enthalpy (b) Entropy
(c) Internal energy (d) Activation energy

Answer: (a) Enthalpy

Enthalpy H = U + PV: the total heat content of a system at constant pressure; ΔH = qp → (a).

Q53 Real gases / Joule–Thomson effect

In the Joule-Thomson expansion of real gas at inversion temperature, the Joule-Thomson coefficient:

(a) will be negative if the gas cools post expansion
(b) will be positive if the gas gets heated post expansion
(c) will be zero if [∂(PV)/ ∂P]T is positive
(d) is zero

Answer: (d) is zero

μJT = (∂T/∂P)H. At the **inversion temperature**, μJT changes sign, so **μJT = 0** → (d). Below Ti gas cools (μ > 0); above it heats (μ < 0). (a) and (b) have the sign rules reversed.

Q54 Thermodynamics / ΔH and ΔU

For $N_2(g) + 3H_2(g) \rightleftharpoons 2\ NH_3(g)$, the expression for ΔH is:

(a) ΔU + 2 RT (b) ΔU + RT
(c) ΔU – 2 RT (d) ΔU – RT

Answer: (c) ΔU – 2 RT

ΔH = ΔU + Δn(g)RT. Δn(g) = 2 – (1 + 3) = **–2** → **ΔH = ΔU – 2RT** → (c).

Q55 Thermodynamics / Trouton-type relation

The entropy of vaporization of a liquid is 100 J $mol^{-1}K^{-1}$ and it boils at 300K. What would be the value of ΔHvap?

(a) 3.0 kJ mol^{-1} (b) 30.0 kJ mol^{-1}
(c) 300 kJ mol^{-1} (d) 3000 kJ mol^{-1}

Answer: (b) 30.0 kJ mol^{-1}

At boiling point, ΔSvap = ΔHvap/Tb → ΔHvap = 100 × 300 = 30,000 J mol^{-1} = **30.0 kJ mol^{-1}** → (b).

Q56 Thermodynamics / Carnot cycle

The maximum efficiency of a Carnot engine operating between 100°C to 200°C will be:

(a) 21.85 % (b) 21.14 %
(c) 22.14 % (d) 20.14%

Answer: (b) 21.14 %

η = (Th – Tc)/Th with **kelvin** temperatures: (473 – 373)/473 = **0.2114 = 21.14%** → (b). Trap: using °C (100/200) gives 50%.

Q57 Thermodynamics / equations of state

Which one of the following is the correct thermodynamic equation of state?

(a) dG = $(\partial G/\partial P)_T\, dP + (\partial G/\partial T)_P\, dT$
(b) $(\partial U/\partial V)_T = P + T(\partial P/\partial T)_V$
(c) dU = $(\partial U/\partial V)_S\, dV + (\partial U/\partial S)_V\, dS$
(d) $(\partial H/\partial P)_T = V - T(\partial V/\partial T)_{P,n}$

Answer: (d) $(\partial H/\partial P)_T = V - T(\partial V/\partial T)_{P,n}$

The **thermodynamic equations of state**: (∂U/∂V)T = T(∂P/∂T)V − P and **(∂H/∂P)T = V − T(∂V/∂T)P** → (d). (b) has the wrong sign. (a) and (c) are just total differentials, not equations of state.

Q58 Thermodynamics / spontaneity

Which one of the following changes will necessarily lead to a non-spontaneous change?

(a) Positive ΔH and positive ΔS
(b) Negative ΔH and negative ΔS
(c) Positive ΔH and negative ΔS
(d) Negative ΔH and positive ΔS

Answer: (c) Positive ΔH and negative ΔS

ΔG = ΔH − TΔS. **ΔH > 0 and ΔS < 0** → ΔG > 0 at **all** temperatures → never spontaneous → (c). (a) spontaneous at high T; (b) at low T; (d) always spontaneous.

Q59 Ionic equilibrium / precipitation

Equal volumes of what concentrations of $AgNO_3$ and HCl should be mixed to form a AgCl precipitate? [Ksp for AgCl = 10^{-10}]

(a) 10^{-4} M $AgNO_3$ and 10^{-7} M HCl
(b) 10^{-5} M $AgNO_3$ and 10^{-6} M HCl
(c) 10^{-6} M $AgNO_3$ and 10^{-6} M HCl
(d) 10^{-4} M $AgNO_3$ and 10^{-5} M HCl

Answer: (d) 10^{-4} M $AgNO_3$ and 10^{-5} M HCl

Equal volumes halve each concentration. Need **ionic product > Ksp = 10^{-10}**. (a) $5\times10^{-5} \times 5\times10^{-8} = 2.5\times10^{-12}$; (b) 2.5×10^{-11}; (c) 2.5×10^{-13}; **(d) $5\times10^{-5} \times 5\times10^{-6} = 2.5\times10^{-10} > 10^{-10}$** → precipitate → (d).

Q60 Ionic equilibrium / Ksp

The solubility product of Ag_2CrO_4 is 32×10^{-12}. What is the concentration of CrO_4^{2-} ion in that solution?

(a) 2×10^{-4} M
(b) 16×10^{-4} M
(c) 8×10^{-4} M
(d) 8×10^{-8} M

Answer: (a) 2×10^{-4} M

$Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^{2-}$. Ksp = $(2s)^2 \cdot s$ = **$4s^3$** = 32×10^{-12} → $s^3 = 8 \times 10^{-12}$ → **$s = 2 \times 10^{-4}$ M** = $[CrO_4^{2-}]$ → (a).

Q61 Solutions / van 't Hoff factor

What will be the degree of dissociation of 0.1 (M) $Ba(NO_3)_2$ solution, if van't Hoff factor of the solution is 2.74?

(a) 91.3 %
(b) 87 %
(c) 100%
(d) 74%

Answer: (b) 87 %

$Ba(NO_3)_2 \rightarrow Ba^{2+} + 2NO_3^-$, n = 3. **$i = 1 + (n - 1)\alpha$** → $2.74 = 1 + 2\alpha$ → **$\alpha = 0.87 = 87\%$** → (b).

Q62 Solutions / colligative properties

Which one of the following colligative properties can provide the most precise molar mass of peptides?

(a) Elevation of boiling point
(b) Depression of freezing point
(c) Relative lowering of vapour pressure
(d) Osmotic pressure

Answer: (d) Osmotic pressure

For **macromolecules** (peptides, proteins, polymers), **osmotic pressure** gives the largest measurable effect even at low concentration, is measured at room temperature (no denaturation) → most precise molar mass → (d).

Q63 Solutions / Raoult's law

At 298 K, the total vapour pressure in Torr for a mixture of volatile components A and B is given by P = 120 – 75χ_B (χ_B is the mole fraction of B). What is the vapour pressure of pure A and B (in Torr) respectively?

(a) 120 and 75
(b) 120 and 195
(c) 120 and 45
(d) 75 and 45

Answer: (c) 120 and 45

P = PA° + (PB° – PA°)χB. Compare with P = 120 – 75χB: **PA° = 120 Torr**; PB° – 120 = −75 → **PB° = 45 Torr** → (c).

Q64 Solutions / colligative relations

Which one of the following equations represents the correct relation between relative lowering in vapour pressure and osmotic pressure (π) for a dilute aqueous solution?

(a) $\frac{\Delta P}{P^0} = \frac{\pi \bar{V}}{RT}$
(b) $\frac{\Delta P}{P^0} = \frac{\pi RT}{\bar{V}}$
(c) $\frac{\Delta P}{P^0} = \frac{\pi R}{T\bar{V}}$
(d) $\frac{\Delta P}{P^0} = \pi RT$

Answer: (a) $\frac{\Delta P}{P^0} = \frac{\pi \bar{V}}{RT}$

Dilute solution: $\Delta P/P° = x_2 \approx n_2/n_1$. Osmotic pressure $\pi = n_2RT/V$ with $V \approx n_1\bar{V}$ ($\bar{V}$ = molar volume of solvent) → $n_2/n_1 = \pi\bar{V}/RT$. So **$\Delta P/P° = \pi\bar{V}/RT$** → (a).

Q65 Solutions / osmotic pressure

A 1% aqueous solution (mass by volume) of a certain substance is isotonic with a 3% solution of glucose (Molar mass = 180 g mol^{-1}) at a given temperature. The molar mass of the substance (in kg mol^{-1}) will be:

(a) 0.60
(b) 180
(c) 0.18
(d) 0.06

Answer: (d) 0.06

Isotonic → **equal molar concentrations** (non-electrolytes). 1 g/100 mL ÷ M = 3 g/100 mL ÷ 180 → M = **60 g mol^{-1} = 0.06 kg mol^{-1}** → (d). Trap: answer asked in kg mol^{-1}.

Q66 Solutions / osmotic pressure

Which among the following is the correct order for osmotic pressure of equimolar solutions of glucose, sodium chloride and barium chloride?

(a) $C_6H_{12}O_6 > BaCl_2 > NaCl$
(b) $C_6H_{12}O_6 > NaCl > BaCl_2$
(c) $BaCl_2 > NaCl > C_6H_{12}O_6$
(d) $NaCl > C_6H_{12}O_6 > BaCl_2$

Answer: (c) $BaCl_2 > NaCl > C_6H_{12}O_6$

π = iCRT; equimolar so π ∝ **i**. $BaCl_2$ i = 3; NaCl i = 2; glucose i = 1 → **$BaCl_2 > NaCl > C_6H_{12}O_6$** → (c).

Q67 Solutions / degree of dissociation

0.05 molal aqueous solution of $K_4[Fe(CN)_6]$ freezes at –0.26°C. Its degree of dissociation will be: (kf =1.86°C Kg mol^{-1})

(a) 48.2 %
(b) 54.9 %
(c) 44.9 %
(d) 51.6 %

Answer: (c) 44.9 %

ΔTf = i Kf m → i = 0.26/(1.86 × 0.05) = **2.796**. $K_4[Fe(CN)_6] \rightarrow 4K^+ + [Fe(CN)_6]^{4-}$, n = 5. α = (i – 1)/(n – 1) = 1.796/4 = **0.449 = 44.9%** → (c).

Q68 Solutions / cryoscopic constant

What will be the value of freezing point depression constant of cyclobutane having freezing point of 280 K and molar enthalpy of fusion of 2.68 kJ mol^{-1}? (Molar mass of cyclobutane = 56.108 g $mol^{-1}$and R= 8.314 $JK^{-1}mol^{-1}$)

(a) 14.63 K kg mol^{-1}
(b) 16.14 K kg mol^{-1}
(c) 13.64 K kg mol^{-1}
(d) 12.64 K kg mol^{-1}

Answer: (c) 13.64 K kg mol^{-1}

$K_f = R T_f^2 M/\Delta H_{fus}$ (M in kg mol^{-1}) = 8.314 × 280^2 × 0.056108 / 2680 = **13.64 K kg mol^{-1}** → (c). Cyclobutane-type solvents have large Kf (like camphor).

Q69 Solutions / Henry's law

Which one of the following statements is correct about the Henry's law?

(a) It is related to effect of pressure only on solubility of a gas in a liquid
(b) It is related to effect of temperature only on solubility of a gas in a liquid
(c) It is related to effect of pressure as well as temperature on solubility of a gas in a liquid
(d) It is related to effect of pressure as well as temperature on solubility of a gas in a solid

Answer: (a) It is related to effect of pressure only on solubility of a gas in a liquid

Henry's law: **p = KH·x** — solubility of a gas in a liquid is **proportional to its partial pressure** at constant temperature → (a). Temperature changes the value of KH, but the law itself states the pressure effect.

Q70 Solutions / Henry's law

What will be the ratio of mole fractions of O_2 and N_2 dissolved in water at 25°C? (Given that Henry's law constant (in torr) for O_2 and N_2 are 3.3 × 10^7 and 6.5 × 10^7 respectively at 25°C; mole fractions of O_2 and N_2 in air are taken as 0.2 and 0.8 respectively)

(a) ~ 0.51
(b) ~0.66
(c) ~0.25
(d) ~0.49

Answer: (d) ~0.49

x = p/KH. $x(O_2)/x(N_2)$ = (0.2/3.3 × 10^7)/(0.8/6.5 × 10^7) = (0.2 × 6.5)/(0.8 × 3.3) = **0.49** → (d). O_2 is about twice as soluble as N_2, so dissolved air is O_2-rich.

Q71 Electrochemistry / conductance

The cell constant with 0.1 N KCl solution is found to be 0.98 cm^{-1} and the resistance offered by 0.01 N HCl is 89 Ω. The specific conductance of HCl will be:

(a) 1.101 × 10^2 Ω^{-1} cm^{-1}
(b) 1.101 × 10^{-2} Ω^{-1} cm^{-1}
(c) 2.202 × 10^{-3} Ω^{-1} cm^{-1}
(d) 2.202 × 10^3 Ω^{-1} cm^{-1}

Answer: (b) 1.101 × 10^{-2} Ω^{-1} cm^{-1}

κ = cell constant / R = 0.98 cm^{-1} / 89 Ω = **1.101 × 10^{-2} Ω^{-1} cm^{-1}** → (b). The cell constant found with KCl applies to any solution in the same cell.

Q72 Electrochemistry / ionic mobility

What will be the correct order of mobility of the following alkali metal ions in aqueous solution?

(a) $Li^+ > Na^+ > K^+ > Rb^+$
(b) $Na^+ > K^+ > Rb^+ > Li^+$
(c) $K^+ > Rb^+ > Na^+ > Li^+$
(d) $Rb^+ > K^+ > Na^+ > Li^+$

Answer: (d) $Rb^+ > K^+ > Na^+ > Li^+$

Smaller ions are **more hydrated**: Li^+ drags the largest water shell, so moves slowest. Mobility: **$Rb^+ > K^+ > Na^+ > Li^+$** → (d). Remember: hydrated size order is the reverse of crystal size.

Q73 Electrochemistry / transport number

During electrolysis of silver nitrate solution, loss in the anode compartment was 0.589 g. In a Voltameter connected in series, 1.259 g of silver was deposited. What would be the transport number of two ions?

(a) $t_+ = 0.468$ and $t_- = 0.532$
(b) $t_+ = 0.532$ and $t_- = 0.468$
(c) $t_+ = 0.670$ and $t_- = 0.330$
(d) $t_+ = 0.330$ and $t_- = 0.670$

Answer: (a) $t_+ = 0.468$ and $t_- = 0.532$

Hittorf method with Ag electrodes: loss of Ag^+ in the **anode compartment** = Ag^+ carried away = $t_+ \times$ total. $t_+ = 0.589/1.259 =$ **0.468**; $t_- = 1 - 0.468 =$ **0.532** → (a).

Q74 Electrochemistry / Kohlrausch's law

The molar conductivities of KOAc and HCl at infinite dilution in water at 25°C are 90.0 and 426.2 S cm² mol⁻¹, respectively. To calculate the molar conductivity of HOAc at infinite dilution, the additional molar conductivity value of which one of the following electrolytes will be required?

(a) NaCl
(b) KCl
(c) KNO_3
(d) NaOH

Answer: (b) KCl

$\Lambda°(HOAc) = \Lambda°(KOAc) + \Lambda°(HCl) - \Lambda°(KCl)$. K^+ and Cl^- cancel. So **KCl** value is needed → (b).

Q75 Electrochemistry / dilution

What will be the effect of dilution on specific and equivalent conductance of an aqueous solution of a strong electrolyte?

(a) The specific conductance decreases and equivalent conductance increases
(b) The specific conductance increases and equivalent conductance decreases
(c) Both will increase
(d) Both will decrease

Answer: (a) The specific conductance decreases and equivalent conductance increases

On dilution: **κ (specific conductance) decreases** — fewer ions per cm³. **Λ (equivalent/molar) increases** — interionic attraction falls and $\Lambda = \kappa \times 1000/c$ → (a).

Q76 Electrochemistry / activity coefficients

The mean ionic activity co-efficient is denoted as γ±, while that of cation and anion are denoted as γ_+ and γ_-, respectively. The correct relation among them will be: (Given that ν_+ and ν_- are the number of cations and the anions respectively in the molecular formula of the compound)

(a) $\gamma_\pm = \frac{1}{\nu_+ + \nu_-}(\gamma_+ + \gamma_-)$
(b) $\gamma_\pm = (\gamma_+^{\nu_+}\gamma_-^{\nu_-})^{1/(\nu_+ + \nu_-)}$
(c) $\gamma_\pm = (\gamma_+^{\nu_-}\gamma_-^{\nu_+})^{1/(\nu_+ + \nu_-)}$
(d) $\gamma_\pm = \frac{1}{\nu_+ + \nu_-}(\nu_+\gamma_+ + \nu_-\gamma_-)$

Answer: (b) $\gamma_\pm = (\gamma_+^{\nu_+}\gamma_-^{\nu_-})^{1/(\nu_+ + \nu_-)}$

Mean ionic activity coefficient is the **geometric mean**: **$\gamma_\pm = (\gamma_+^{\nu_+}\gamma_-^{\nu_-})^{1/(\nu_+ + \nu_-)}$** → (b). Example: for $CaCl_2$, $\gamma_\pm^3 = \gamma_+\gamma_-^2$.

Q77 Electrochemistry / degree of dissociation

The specific conductance of 0.01 M solution of acetic acid was found to be 0.015 S m^{-1} at 25°C. Molar conductance of acetic acid at infinite dilution is 400 × 10^{-4} S m^2 mol^{-1}. The degree of dissociation of acetic acid will be:

(a) 0.375
(b) 0.0375
(c) 0.00375
(d) 0.357

Answer: (b) 0.0375

$\Lambda m = \kappa/c$ = 0.015 S m^{-1} / 10 mol m^{-3} = **1.5 × 10^{-3} S m^2 mol^{-1}**. $\alpha = \Lambda m/\Lambda°m$ = 1.5 × 10^{-3} / 400 × 10^{-4} = **0.0375** → (b). Trap: 0.01 M = 10 mol m^{-3}.

Q78 Electrochemistry / moving boundary

In a moving boundary experiment with 0.01 mole LiCl, the boundary in a tube with cross sectional area of 0.125 cm^2 moves through 8.1 cm in 1500 sec for a current of 1.8 × 10^{-3} ampere. What will be the value of transport number of Cl^-? (Given that F = 96,500 Coulomb and temperature is 300K)

(a) 0.639
(b) 0.361
(c) 0.510
(d) 0.369

Answer: (a) 0.639

The boundary measures the cation: **$t(Li^+) = cFAl/(It)$** = (1 × 10^{-5} mol cm^{-3} × 96500 × 0.125 × 8.1)/(1.8 × 10^{-3} × 1500) = **0.362**. **$t(Cl^-) = 1 - 0.362 = 0.638 \approx 0.639$** → (a).

Q79 Electrochemistry / conductometric titration

When HCl is titrated against NaOH, the conductance at the end point is:

(a) Zero
(b) Minimum
(c) Maximum
(d) Infinite

Answer: (b) Minimum

Fast H^+ ($\lambda° \approx 350$) is replaced by slow Na^+ (≈ 50): conductance **falls** to the end point, then rises as excess OH^- (≈ 198) is added. V-shaped curve → **minimum at the end point** → (b).

Q80 Solutions / tonicity

A cell is bathed in a solution that has a greater osmolarity than that of cytosol. The solution can be described as:

(a) Hypertonic
(b) Hypotonic
(c) Isotonic
(d) Hydrotonic

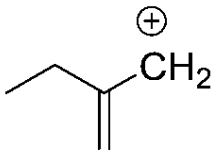
Answer: (a) Hypertonic

Outside solution has **higher osmolarity** than the cytosol → **hypertonic**; water leaves the cell, which shrinks (plasmolysis/crenation) → (a).

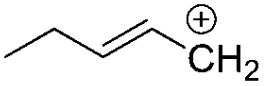
Q81 Organic / carbocation stability

Which cationic species is more stable in each of the following pairs?

Pair X:

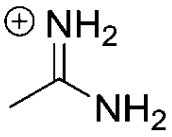


1

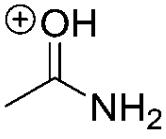


2

Pair Y:



3



4

(a) 1 and 3
(b) 1 and 4
(c) 2 and 4
(d) 2 and 3

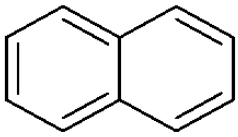
Answer: (d) 2 and 3

Pair X: 1 is a primary allylic cation conjugated only with $C=CH_2$ ending in CH_2; **2** (pent-2-enyl) delocalises + onto a **secondary** carbon → more stable. Pair Y: **3** (protonated amidine) is stabilised by **two NH_2 donors**, while 4 (protonated amide) has one NH_2 and OH (O less donating). → 2 and 3 → (d).

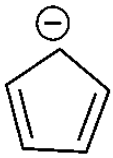
Q82 Organic / aromaticity

Which one of the following structures is non-aromatic?

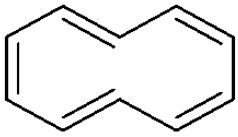
(a)



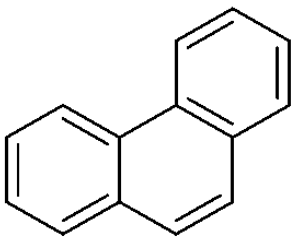
(b)



(c)



(d)



Answer: (c)

Naphthalene (10π) and phenanthrene (14π) are aromatic; cyclopentadienyl anion (6π) is aromatic. **[10]Annulene** (cyclode-

capentaene) cannot be planar — inner H atoms clash (or angle strain) — so it is **non-aromatic** → (c).

Q83 Organic / hyperconjugation

The o/p-directing effect of methyl group in electrophilic substitution reaction of toluene is due to:

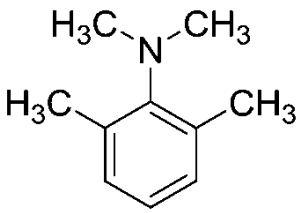
(a) Inductive effect
(b) Hyperconjugation effect
(c) Resonance effect
(d) Electromeric effect

Answer: (b) Hyperconjugation effect

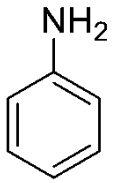
CH_3 has no lone pair or π bond to give classical resonance. Its σ(C–H) electrons overlap with the ring π system (**hyperconjugation**, no-bond resonance), raising electron density at **ortho and para** → (b). Inductive (+I) effect is weaker and less position-specific.

Q84 Organic / basicity of amines

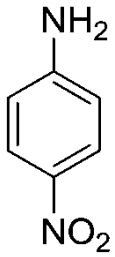
The relative order of basicity of the following amines is:



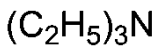
1



2



3



4

(a) 1 > 2 > 3 > 4
(b) 4 > 1 > 2 > 3
(c) 4 > 3 > 2 > 1
(d) 2 >3 > 1 > 4

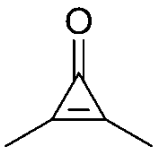
Answer: (b) 4 > 1 > 2 > 3

4 Et_3N: aliphatic, sp^3 lone pair free → most basic. 1: two ortho CH_3 twist NMe_2 out of the ring plane (**steric inhibition of resonance**) → lone pair not delocalised → more basic than aniline. 2 aniline > 3 p-nitroaniline (−R of NO_2). **4 > 1 > 2 > 3** → (b).

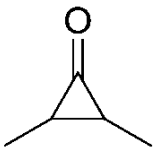
Q85 Organic / dipole moment and aromaticity

Which molecule in each of the following pairs has a higher dipole moment?

Pair X:

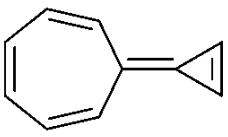


1

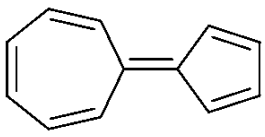


2

Pair Y:



3



4

(a) 1 and 3
(b) 1 and 4
(c) 2 and 3
(d) 2 and 4

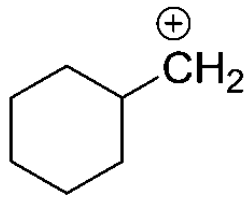
Answer: (b) 1 and 4

Pair X: **1 cyclopropenone** — C=O polarises to give an aromatic 2π cyclopropenium ring → large dipole (> 4 D); 2 (cyclopropanone) cannot. Pair Y: **4** (calicene-type sesquifulvalene) separates charge into **tropylium$^+$ (6π)** and **cyclopentadienide$^-$ (6π)**, both aromatic → larger dipole. → 1 and 4 → (b).

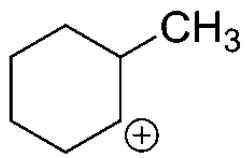
Q86 Organic / carbocation rearrangement

Which one of the following carbocations is NOT expected to rearrange?

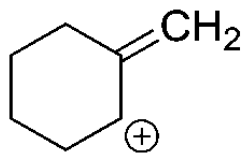
(a)



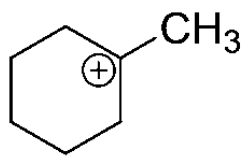
(b)



(c)



(d)



Answer: (d)

Rearrangement happens only if a **more stable** cation can form. (a) 1° cyclohexylmethyl → shifts/ring-expands. (b) 2° next to a 3° C–H → hydride shift to 3°. (c) allylic, delocalised. **(d) 1-methylcyclohexyl is tertiary**; no shift gives a more stable ion → does not rearrange → (d).

Q87 Organic / reagents

Classify the following species as electrophiles (E) and nucleophiles (N) in organic reactions: SO_3, Cl^+, NO_2^+, CH_3NH_2, H_3O^+, BH_3, CN^-

(a) E = SO_3, Cl^+, NO_2^+, H_3O^+ and N = BH_3, CH_3NH_2, CN^-
(b) E = Cl^+, NO_2^+, H_3O^+ and N = SO_3, BH_3, CH_3NH_2, CN^-
(c) E = SO_3, BH_3, Cl^+, NO_2^+, H_3O^+ and N = CH_3NH_2, CN^-
(d) E = CH_3NH_2, NO_2^+, H_3O^+, Cl^+ and N = SO_3, BH_3, CN^-

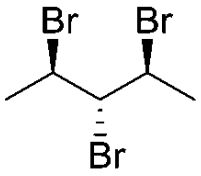
Answer: (c) E = SO_3, BH_3, Cl^+, NO_2^+, H_3O^+ and N = CH_3NH_2, CN^-

Electrophiles (electron-poor, empty orbital or + centre): **SO_3, BH_3, Cl^+, NO_2^+, H_3O^+**. **Nucleophiles** (lone pair): **CH_3NH_2, CN^-** → (c). Trick: BH_3 and SO_3 are neutral but electron-deficient.

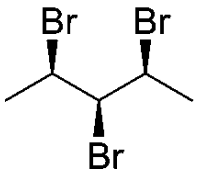
Q88 Stereochemistry / meso compounds

Which one of the following molecules does NOT exist as a meso isomer?

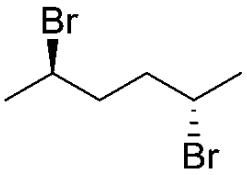
(a)



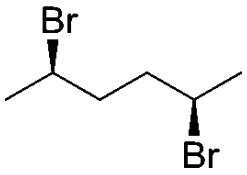
(b)



(c)



(d)



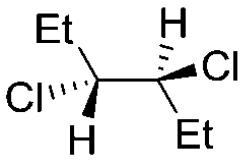
Answer: (d)

Meso needs two (or more) stereocentres with **internal mirror symmetry**. 2,3,4-Tribromopentane (a, b) and 2,5-dibromohexane drawn (c) are meso forms. **(d)** 2,5-dibromohexane with **both Br wedged** in this zigzag is the (R,R)/(S,S) form → **chiral**, no meso → (d).

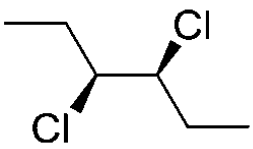
Q89 Stereochemistry / symmetry elements

Which one of the following molecules does NOT have a plane of symmetry?

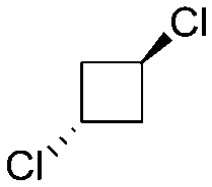
(a)



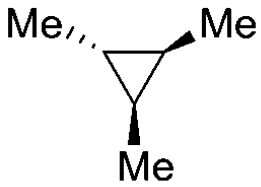
(b)



(c)



(d)



Answer: (b)

(b) 3,4-dichlorohexane as drawn is **(3S,4S)** — a chiral (dl) form, so it has **no plane of symmetry**. (a) is the meso form, (c) trans-1,3-dichlorocyclobutane and (d) the trimethylcyclopropane have a mirror plane → (b).

Q90 Biomolecules / amino acids

Which one of the following amino acids is achiral?

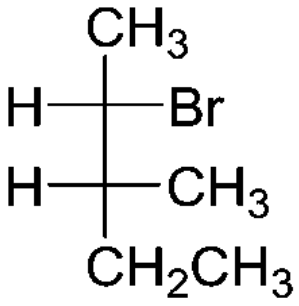
(a) Alanine
(b) Glycine
(c) Proline
(d) Valine

Answer: (b) Glycine

Glycine $H_2N–CH_2–COOH$: the α-carbon carries **two H** → not a stereocentre → **achiral**. All other standard amino acids are chiral → (b).

Q91 Stereochemistry / Fischer projections

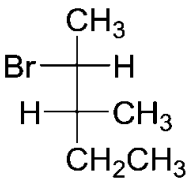
Consider the following compound [A]:



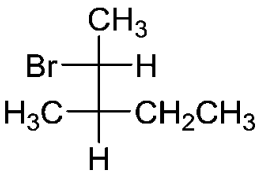
[A]

Which one of the following represents an enantiomer of [A]?

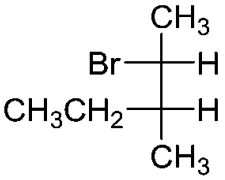
(a)



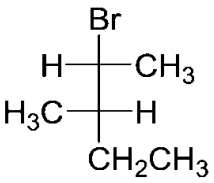
(b)



(c)



(d)

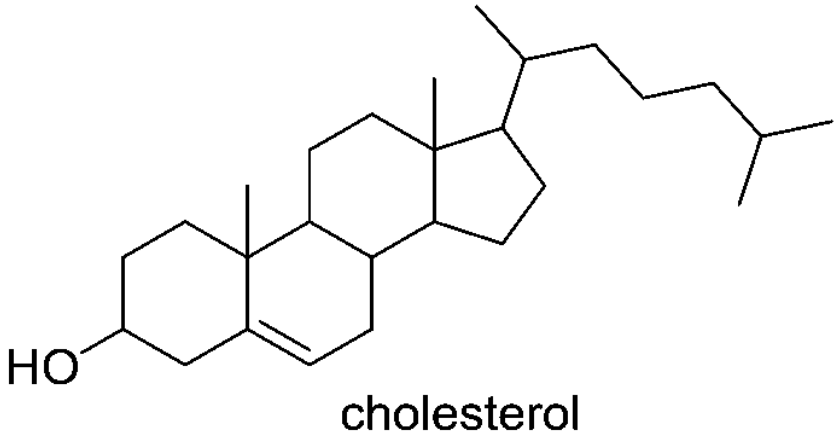


Answer: (d)

[A] is **(2S,3R)**-2-bromo-3-methylpentane. Enantiomer must invert **both** centres → **(2R,3S)**. Assigning CIP to options: (a) 2R,3R; (b) 2R,3R; (c) 2R,3R; **(d) 2R,3S** → (d). Trick: lowest priority (H) on a horizontal bond → reverse the observed sense.

Q92 Stereochemistry / counting isomers

The total number of optical isomers possible for cholesterol is:



cholesterol

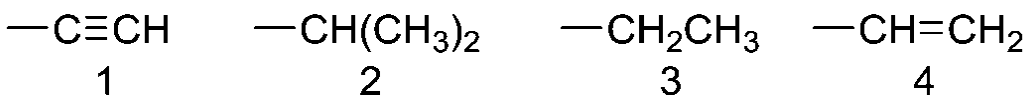
(a) 128
(b) 256
(c) 64
(d) 512

Answer: (b) 256

Cholesterol has **8 stereocentres** (C3, C8, C9, C10, C13, C14, C17, C20). Maximum stereoisomers = 2^8 = **256** → (b). Only one occurs naturally.

Q93 Stereochemistry / CIP rules

Consider the following groups attached to a chiral carbon centre:



What is the decreasing order of priority of above groups based on Cahn-Ingold-Prelog (CIP)- nomenclature?

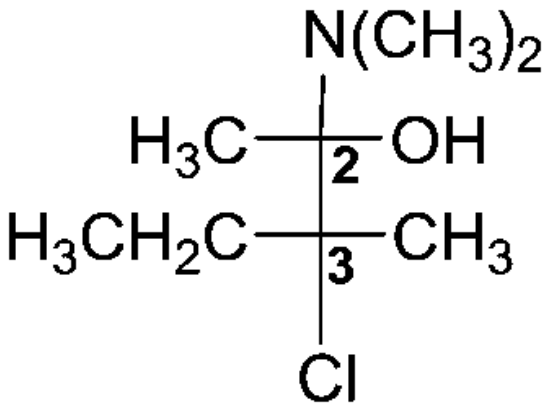
(a) 1 > 4 > 2 > 3
(b) 1 > 2 > 3 >4
(c) 2 > 1 > 4 > 3
(d) 4 > 1 > 3 > 2

Answer: (a) 1 > 4 > 2 > 3

First atoms all C. Substituent sets: **−C≡CH (C,C,C)** highest. −CH=CH_2 (C,C,H) and −$CH(CH_3)_2$ (C,C,H) tie; go one step further: vinyl's duplicated C gives (C,H,H) vs isopropyl (H,H,H) → **vinyl > isopropyl**. −CH_2CH_3 (C,H,H) lowest. **1 > 4 > 2 > 3** → (a).

Q94 Stereochemistry / R and S

What is the correct configuration of C2 and C3 carbons in the following compound?



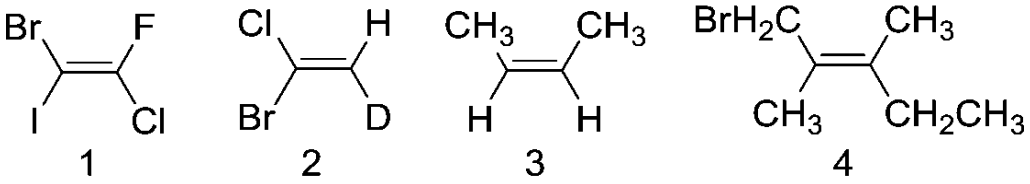
(a) 2R, 3S
(b) 2S, 3R
(c) 2R, 3R
(d) 2S, 3S

Answer: (c) 2R, 3R

C2: OH > $N(CH_3)_2$ > C3 (Cl,C,C) > CH_3. C3: Cl > C2 (O,N,C) > CH_2CH_3 > CH_3. In both, lowest priority sits on a **horizontal** bond, so reverse the drawn sense: C2 → **R**, C3 → **R** → (c).

Q95 Stereochemistry / E–Z

The E/Z-nomenclature for the following molecules is:



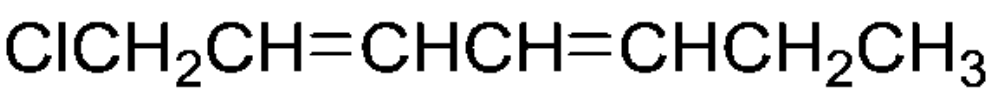
(a) 1: Z, 2: Z, 3: Z, 4: E
(b) 1: Z, 2: E, 3: E, 4: E
(c) 1: E, 2: Z, 3: Z, 4: E
(d) 1: E, 2: Z, 3: E, 4: Z

Answer: (a) 1: Z, 2: Z, 3: Z, 4: E

1: I > Br and Cl > F; I and Cl same side → **Z**. 2: Br > Cl and D > H; Br and D same side → **Z**. 3: cis-but-2-ene → **Z**. 4: CH_2Br > CH_3 (top left) and CH_2CH_3 > CH_3 (bottom right) → opposite → **E** → (a).

Q96 Stereochemistry / counting isomers

The total number of stereoisomers possible for the given compound is:



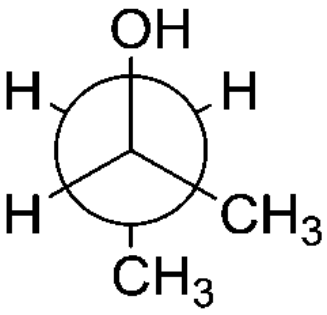
(a) 4
(b) 6
(c) 8
(d) 10

Answer: (a) 4

$ClCH_2CH{=}CH{-}CH{=}CHCH_2CH_3$ has **two stereogenic C=C** with different ends (no stereocentre). Unsymmetrical, so 2^2 = **4** (EE, EZ, ZE, ZZ) → (a).

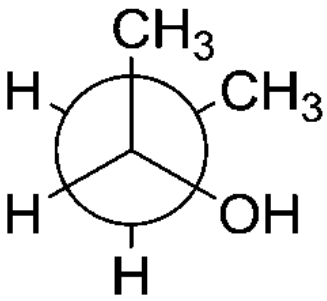
Q97 Stereochemistry / Newman projections

Two compounds [X] and [Y] are given below:



[X]

and



[Y]

The relationship between [X] and [Y] is:

(a) Identical
(b) Diastereomers
(c) Enantiomers
(d) Constitutional isomers

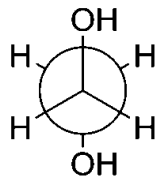
Answer: (c) Enantiomers

Both are butan-2-ol. On the stereocentre, H and the ethyl carbon keep their places while **OH and CH_3 swap** between [X] and [Y]. One swap = inverted configuration → **enantiomers** → (c).

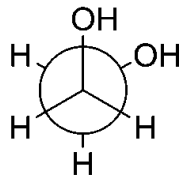
Q98 Conformations / ethylene glycol

Which one of the following is the most stable conformation of ethylene glycol?

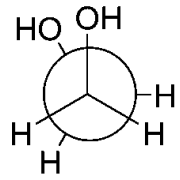
(a)



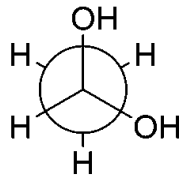
(b)



(c)



(d)

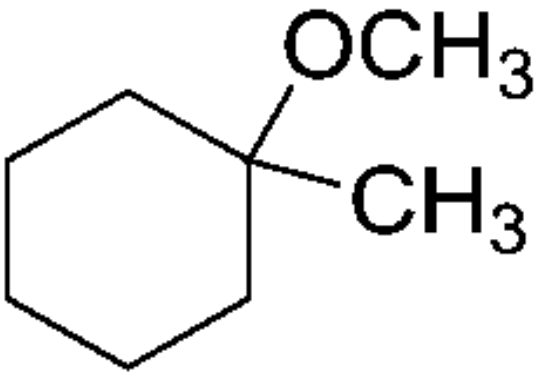


Answer: (b)

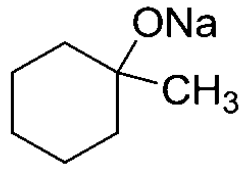
In $HOCH_2CH_2OH$ the **gauche** conformer is most stable: the two OH groups at 60° form an **intramolecular H-bond**, outweighing gauche strain. Option (b) shows OH/OH gauche → (b). (Same for 2-fluoroethanol.)

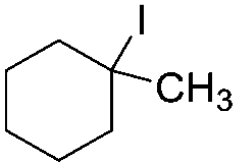
Q99 Organic synthesis / Williamson ether

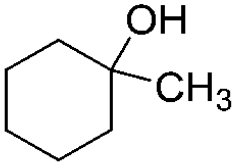
Consider the following compound:

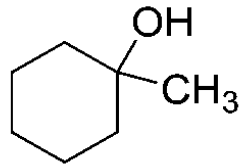


Which one of the following substrate sets is the best for synthesizing above compound?

(a) CH_3I + 

(b) CH_3ONa + 

(c) CH_3OH + 

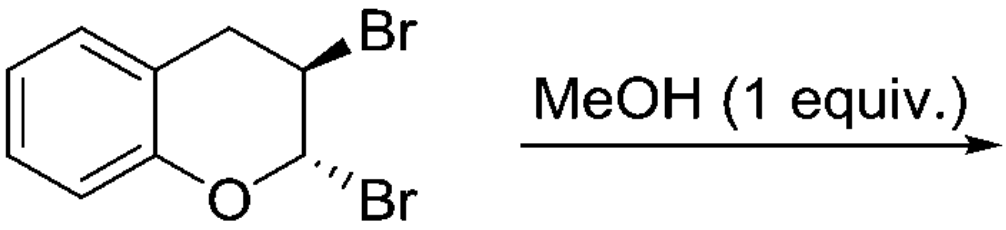
(d) CH_3I + 

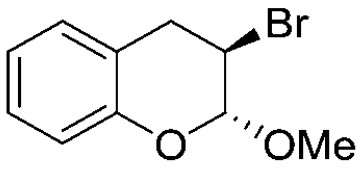
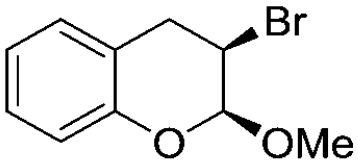
Answer: (a)

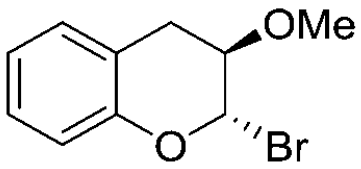
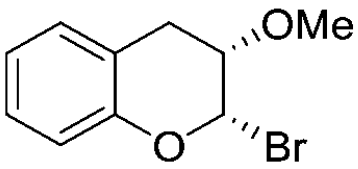
Williamson synthesis is **SN2**: the halide must be **methyl/primary**. A tertiary halide with CH_3O^- would give **elimination** (alkene). So use **CH_3I + tertiary alkoxide** (1-methylcyclohexan-1-olate) → (a).

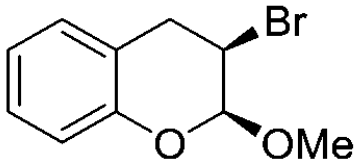
Q100 Organic / SN1 at anomeric carbon

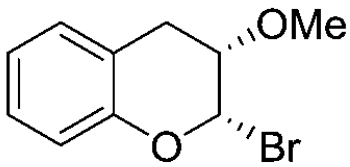
The major product(s) formed in the following reaction is/are:



(a)  and 

(b)  and 

(c)  only

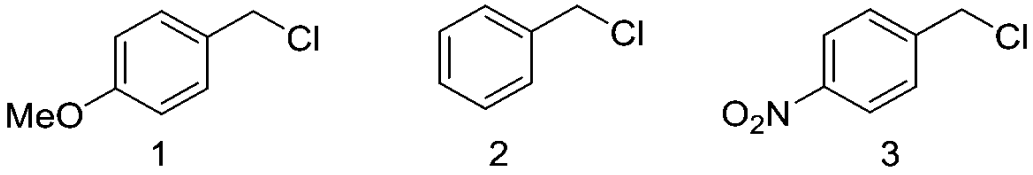
(d)  only

Answer: (a)

C2–Br sits next to ring O: it ionises easily (**oxocarbenium ion**, SN1). MeOH attacks the planar cation from **both faces** → both C2 epimers with **OMe**; the C3–Br (ordinary 2°) is untouched with 1 equiv. MeOH → (a).

Q101 Organic / SN1 reactivity

The relative order of reactivity of the following chlorides in SN1 reaction is:



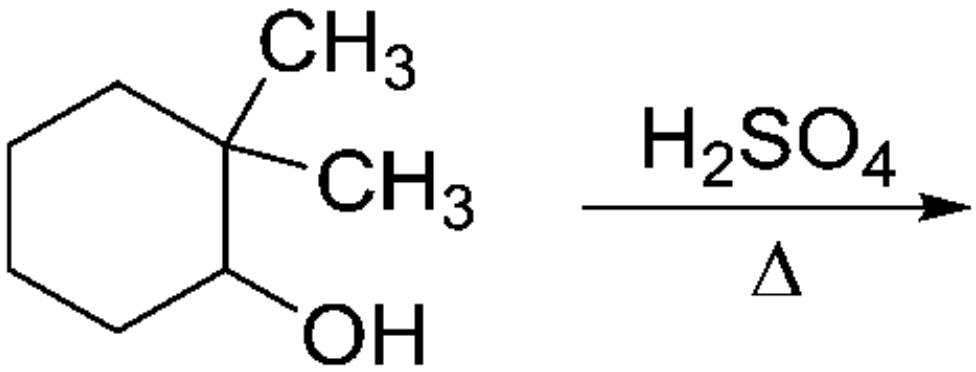
(a) 2 > 1 > 3
(b) 3 > 2 > 1
(c) 1 > 2 > 3
(d) 1 > 3 > 2

Answer: (c) 1 > 2 > 3

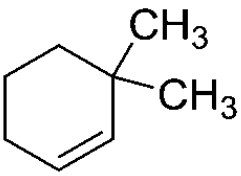
SN1 rate follows **benzyl cation stability**. p-OMe (+R) stabilises most; p-NO_2 (−R, −I) destabilises. **1 > 2 > 3** → (c).

Q102 Organic / dehydration with rearrangement

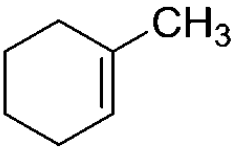
The major product formed in the following reaction is:



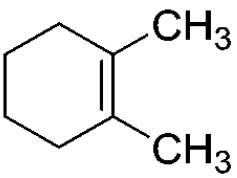
(a)



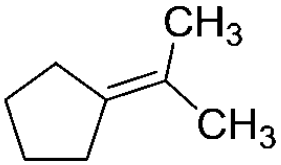
(b)



(c)



(d)

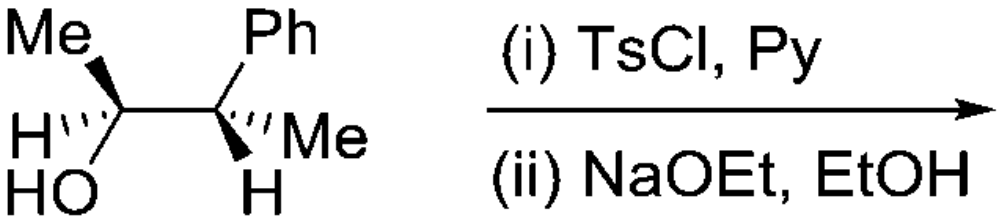


Answer: (c)

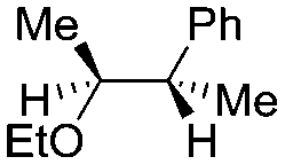
2,2-Dimethylcyclohexanol + H_2SO_4: 2° cation forms, then **1,2-methyl shift** gives a **3° cation**; loss of H^+ gives the most substituted alkene, **1,2-dimethylcyclohexene** (tetrasubstituted, Saytzeff) → (c). Ring contraction to (d) is minor.

Q103 Organic / E2 stereochemistry

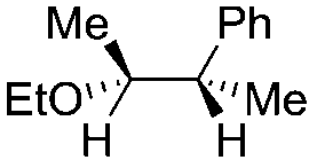
The major product formed in the following reaction is:



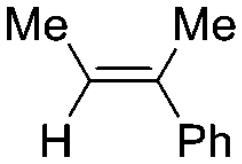
(a)



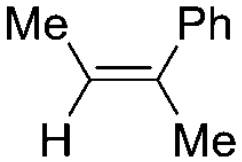
(b)



(c)



(d)



Answer: (c)

TsCl/py converts OH to **OTs with retention** (C–O not broken). NaOEt then does **anti-periplanar E2**: placing C3–H anti to OTs puts the two Me groups on the same side and Ph cis to H → alkene (c). E2 is **stereospecific**.

Q104 Organic / E2 elimination

Which one of the following bromides CANNOT form an alkene by E2 process?

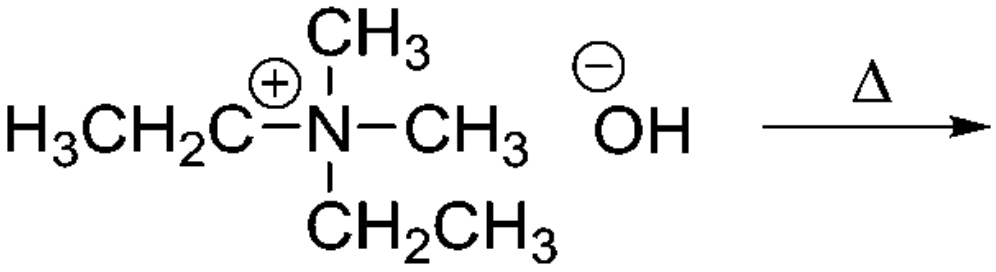
(a) 1-Bromo-2,2-dimethylpropane
(b) 2-Bromo-2-methylbutane
(c) 2-Bromo-3-methylbutane
(d) 1-Bromo-3-methylbutane

Answer: (a) 1-Bromo-2,2-dimethylpropane

E2 needs a **β-hydrogen**. **1-Bromo-2,2-dimethylpropane** (neopentyl bromide, $(CH_3)_3C–CH_2Br$): the β-carbon is quaternary, **no β-H** → cannot form an alkene by E2 → (a).

Q105 Organic / Hofmann elimination

The major product formed in the following reaction is:



(a) $CH_3CH{=}CH_2$

(b) $CH_3CH{=}CHCH_3$

(c) $CH_3CH_2CH{=}CH_2$

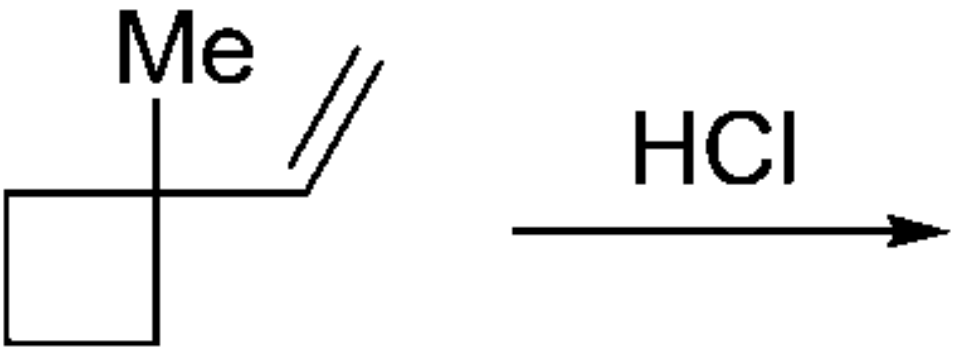
(d) $H_2C{=}CH_2$

Answer: (d)

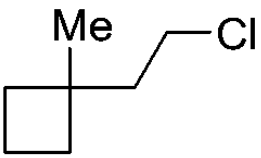
Quaternary ammonium hydroxide on heating gives the **Hofmann product** (least substituted alkene) — OH^- removes the most accessible, most acidic β-H. Here the ethyl group gives **ethene, $H_2C{=}CH_2$** → (d).

Q106 Organic / ring expansion

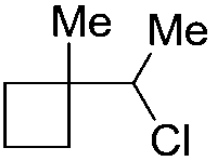
The major product formed in the following reaction is:



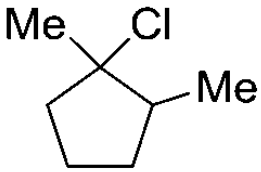
(a)



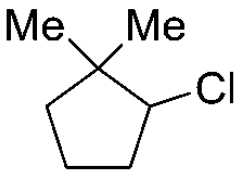
(b)



(c)



(d)



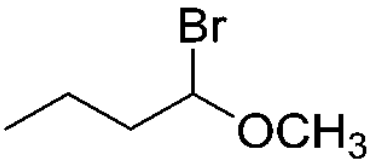
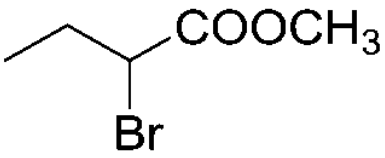
Answer: (c)

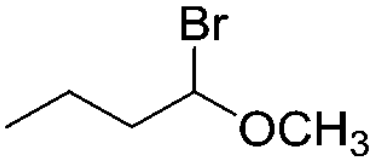
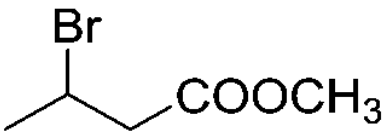
HCl adds Markovnikov: secondary cation next to the strained cyclobutane. **Ring expansion** (C–C shift) relieves strain and gives a **tertiary cyclopentyl cation** carrying CH_3; Cl^- traps it → **1-chloro-1,2-dimethylcyclopentane** → (c).

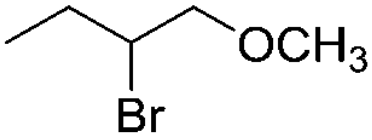
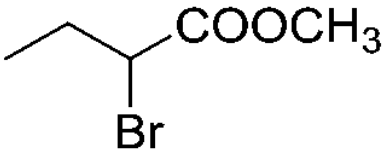
Q107 Organic / regioselective HBr addition

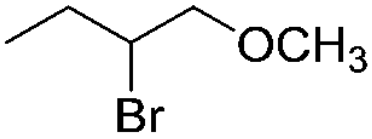
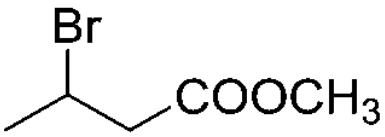
The major products [X] and [Y] formed in the following transformations are:



(a) [X] =  [Y] = 

(b) [X] =  [Y] = 

(c) [X] =  [Y] = 

(d) [X] =  [Y] = 

Answer: (b)

[X]: enol ether — H^+ adds to C2, + at C1 is stabilised by O (**oxocarbenium**) → Br on the carbon bearing **OCH_3**. [Y]: α,β-unsaturated ester — **conjugate (1,4) addition**; Br^- ends on the **β-carbon** → (b).

Q108 Organic / peroxide effect

The major product formed in the reaction of 3-phenylpropene with HBr in the presence of peroxide is:

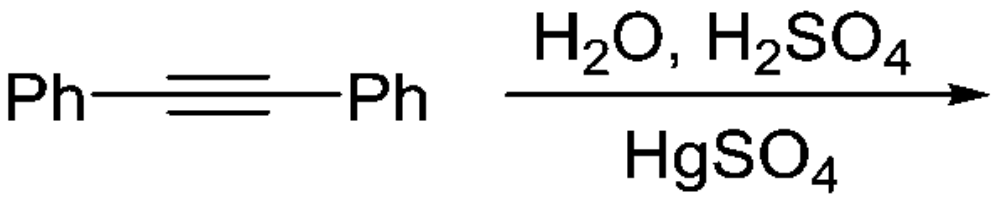
(a) 2-Bromo-1-phenylpropane
(b) 1,2-Dibromo-3-phenylpropane
(c) 1-Bromo-3-phenylpropane
(d) 3-(p-Bromophenyl) propene

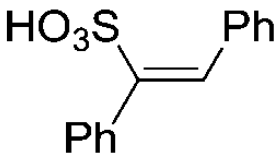
Answer: (c) 1-Bromo-3-phenylpropane

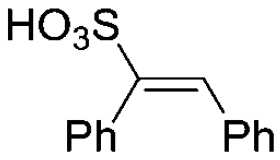
HBr + **peroxide** → free-radical, **anti-Markovnikov** addition. Br• adds to terminal CH_2 to give the more stable 2° radical: $PhCH_2CH{=}CH_2$ → **$PhCH_2CH_2CH_2Br$** = 1-bromo-3-phenylpropane → (c).

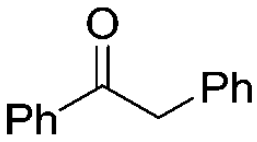
Q109 Organic / alkyne hydration

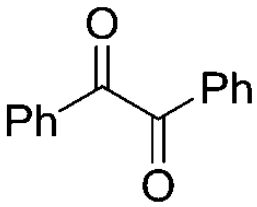
The major product formed in the following reaction is:



(a) 

(b) 

(c) 

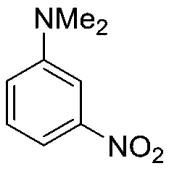
(d) 

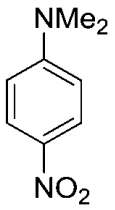
Answer: (c)

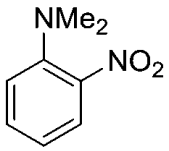
Hg^{2+}/H_2SO_4 hydration of an alkyne gives an **enol → ketone** (tautomerism). Diphenylacetylene → **$PhCOCH_2Ph$** (deoxybenzoin) → (c).

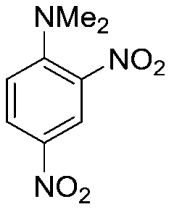
Q110 Organic / nitration of amines

The major product formed in the reaction of N,N-dimethylaniline with concentrated H_2SO_4/HNO_3 mixture is:

(a) 

(b) 

(c) 

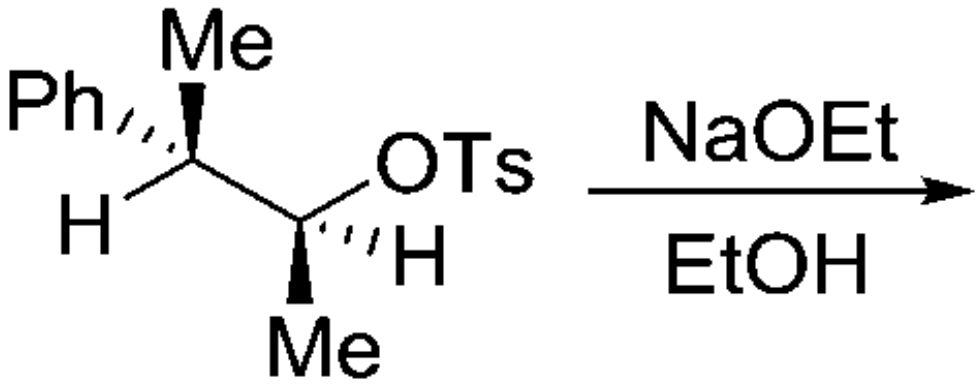
(d) 

Answer: (a)

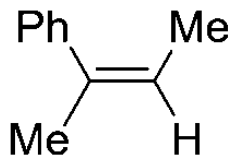
In conc. H_2SO_4/HNO_3 the NMe_2 group is **protonated** to $-N^+HMe_2$, a strong **meta-director** (−I). Major product **m-nitro-N,N-dimethylaniline** → (a).

Q111 Organic / E2 stereochemistry

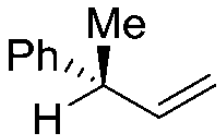
The major product formed in the following reaction is:



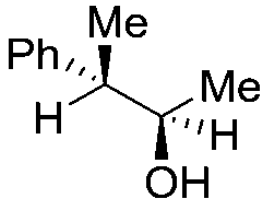
(a)



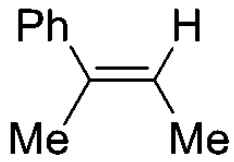
(b)



(c)



(d)

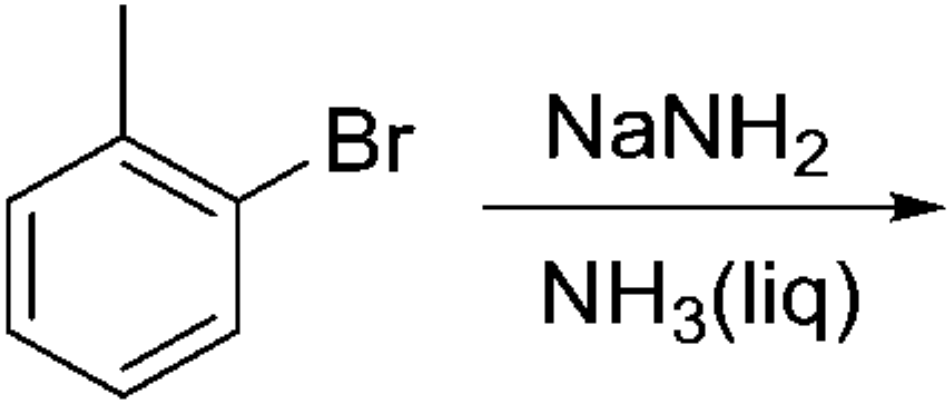


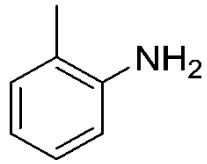
Answer: (d)

NaOEt/EtOH on a 2° tosylate → **anti-periplanar E2**. Rotating C3–OTs anti to C2–H places **Me and Me cis**, Ph cis to H → (E)-2-phenylbut-2-ene drawn in (d) → (d). Remember: E2 is stereospecific.

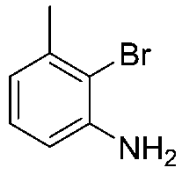
Q112 Organic / benzyne mechanism

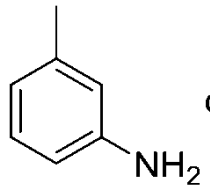
The major product(s) formed in the following reaction is/are:



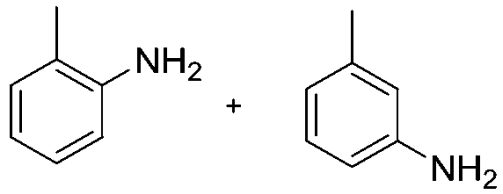
(a) 

only

(b) 

(c) 

only

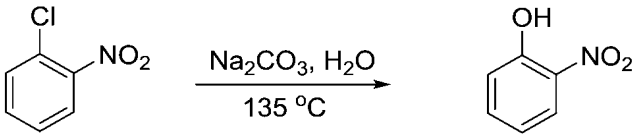
(d) 

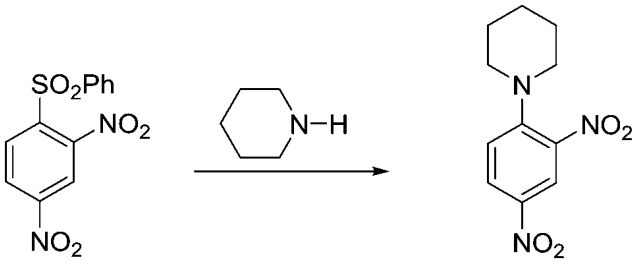
Answer: (a)

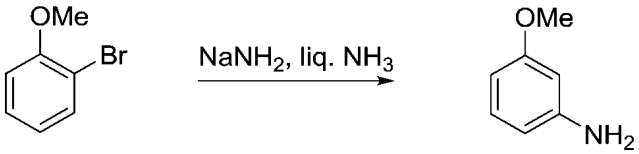
$NaNH_2$/liq. NH_3 on o-bromotoluene goes by **elimination–addition (benzyne)**: 3-methylbenzyne forms and NH_2^- adds to either end. Strictly this gives a **mixture of o- and m-toluidine** (option d). UPSC's key holds (a).

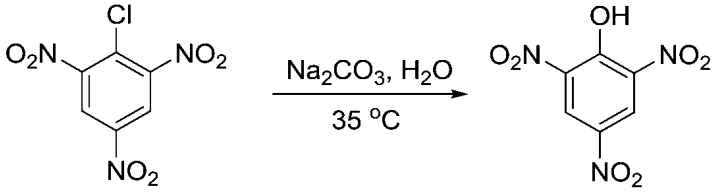
Q113 Organic / ipso substitution

Which one of the following reactions is NOT an example of ipso-substitution?

(a) 

(b) 

(c) 

(d) 

Answer: (c)

Ipso = the nucleophile enters the carbon that **carried the leaving group**. (a), (b), (d) are SNAr at that carbon. (c) goes via **benzyne**: NH_2 enters the **adjacent** carbon (cine substitution) → NOT ipso → (c).

Q114 Organic / side-chain halogenation

The product formed by the reaction of toluene with chlorine in the presence of sunlight is:

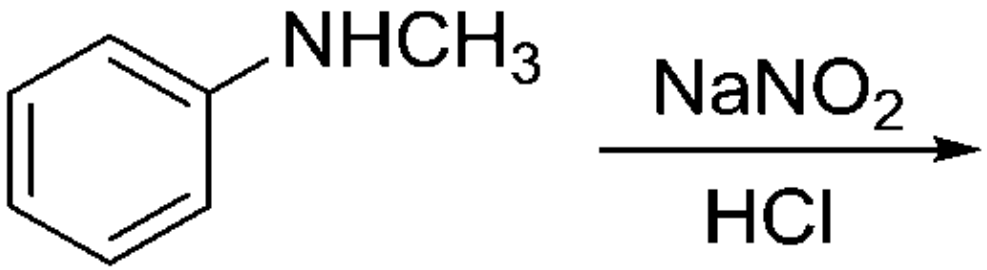
(a) o-chlorotoluene
(b) 2,4-dichlorotoluene
(c) p-chlorotoluene
(d) benzylchloride

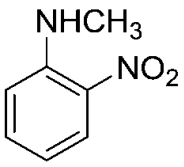
Answer: (d) benzylchloride

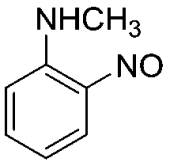
Cl_2 in **sunlight (hv)**, no Lewis acid → **free-radical** substitution at the **benzylic** C–H → **benzyl chloride** $C_6H_5CH_2Cl$ → (d). With $FeCl_3$ (dark) → o/p-chlorotoluene.

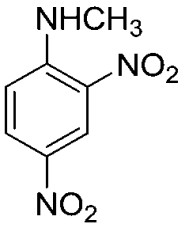
Q115 Organic / secondary amines with HNO_2

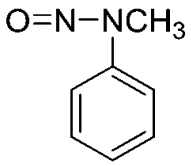
The major product formed in the following reaction is:



(a)


(b)


(c)


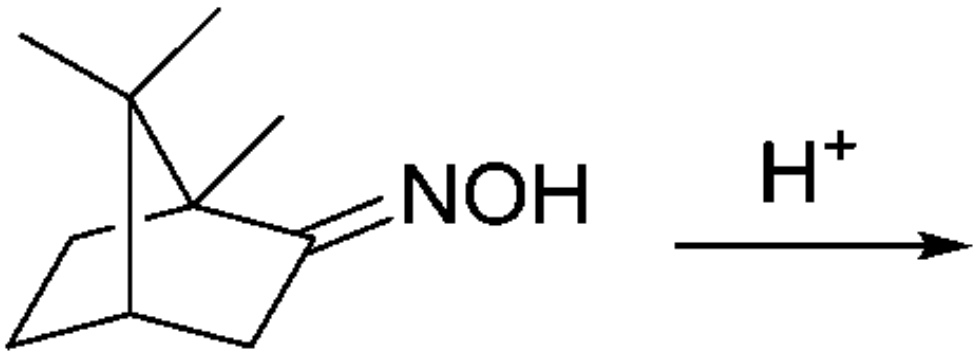
(d)


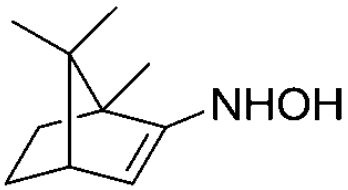
Answer: (d)

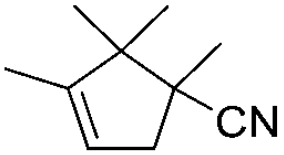
Secondary amines react with HNO_2 ($NaNO_2$/HCl) to give **N-nitrosoamines** (yellow oil): $C_6H_5N(CH_3)–N=O$ → (d). (Liebermann nitroso test.)

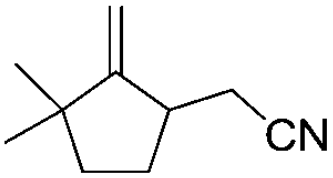
Q116 Organic / Beckmann fragmentation

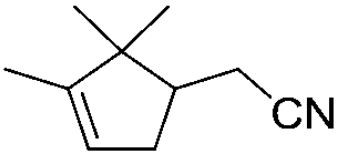
The major product formed in the following reaction is:



(a) 

(b) 

(c) 

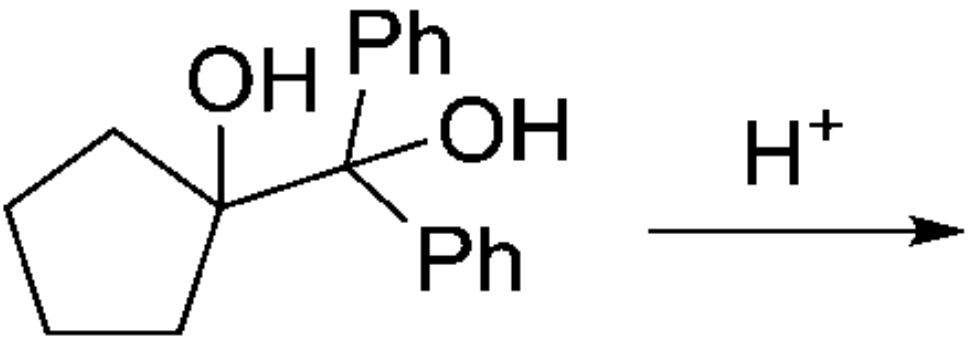
(d) 

Answer: (d)

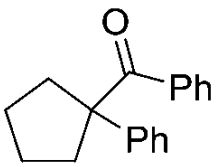
Camphor oxime + acid: the C–C bond anti to OH can break to give a stable **tertiary cation** instead of normal Beckmann migration → **fragmentation** to a nitrile; loss of H^+ gives the alkene: **α-campholenonitrile** → (d).

Q117 Organic / pinacol rearrangement

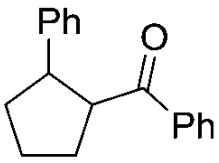
The major product formed in the following reaction is:



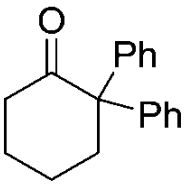
(a)



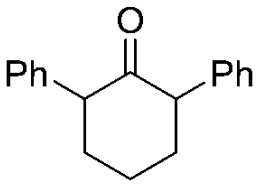
(b)



(c)



(d)

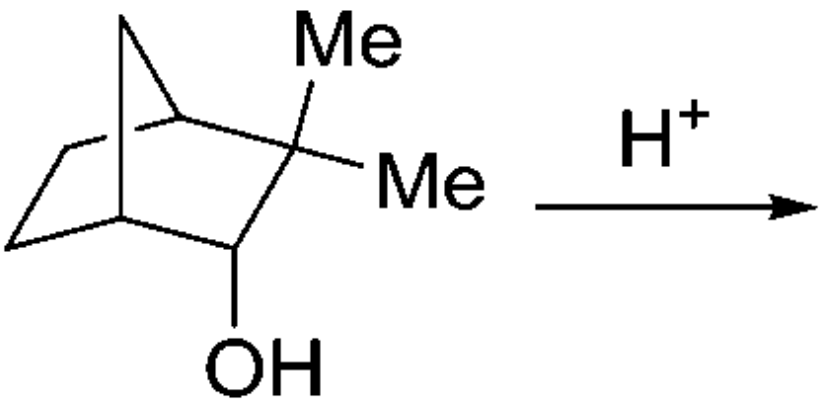


Answer: (c)

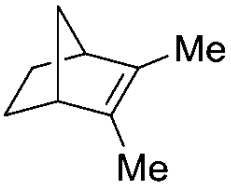
Ionisation gives the more stable **diphenyl-stabilised cation**. A **ring C–C bond migrates** to it (ring expansion 5 → 6), and the ring oxygen becomes C=O → **2,2-diphenylcyclohexanone** → (c).

Q118 Organic / Wagner–Meerwein rearrangement

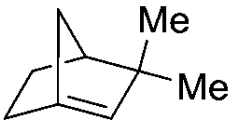
The major product formed in the following reaction is:



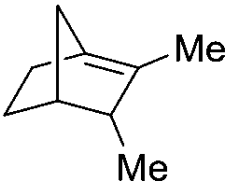
(a)



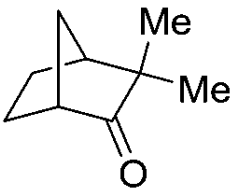
(b)



(c)



(d)

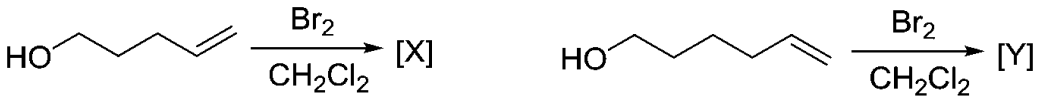


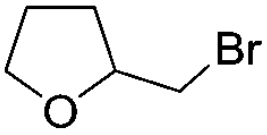
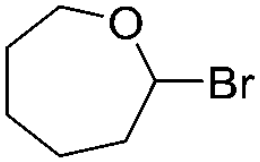
Answer: (a)

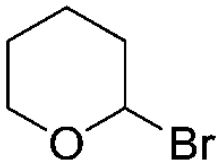
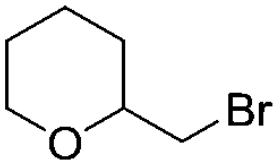
Protonation and loss of water at C2 next to the gem-dimethyl carbon → **1,2-methyl shift** gives a **tertiary** cation; loss of H^+ gives the tetrasubstituted alkene **2,3-dimethylnorborn-2-ene** → (a).

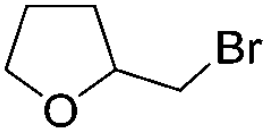
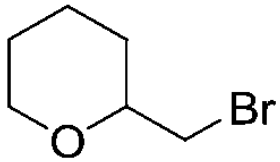
Q119 Organic / halo-etherification

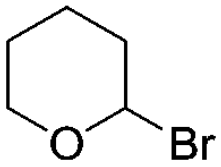
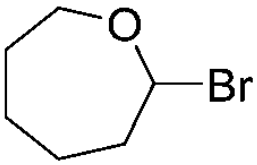
The major products [X] and [Y] formed in the following reactions are:



(a) [X] =  [Y] = 

(b) [X] =  [Y] = 

(c) [X] =  [Y] = 

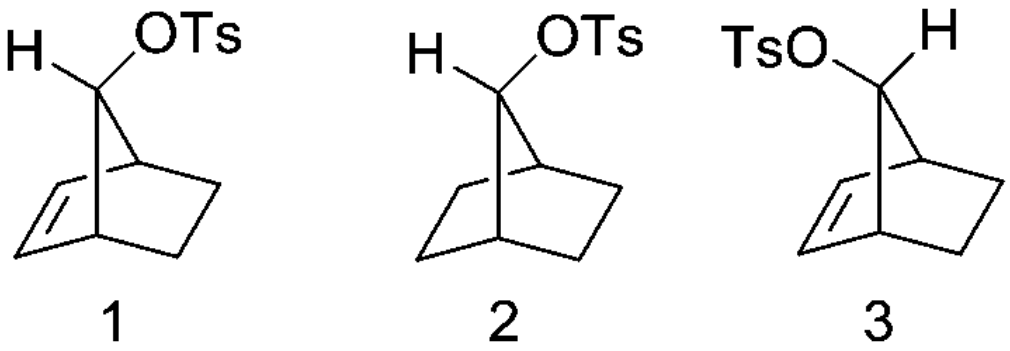
(d) [X] =  [Y] = 

Answer: (c)

Br_2 forms a bromonium ion; the OH attacks intramolecularly. Pent-4-en-1-ol → **5-exo** → 2-(bromomethyl)**tetrahydrofuran** [X]. Hex-5-en-1-ol → **6-exo** → 2-(bromomethyl)**tetrahydropyran** [Y] → (c). Exo closure is favoured (Baldwin).

Q120 Organic / neighbouring group participation

The relative order of the rate of acetolysis among the following norbornyl derivatives is:



(a) 1 > 2 > 3
(b) 1 > 3 > 2
(c) 3 > 2 > 1
(d) 3 > 1 > 2

Answer: (b) 1 > 3 > 2

1 = anti-7-norbornenyl tosylate: C=C π electrons sit directly behind the C–OTs bond and assist ionisation → ~10^{11} times faster than saturated **2**. **3 (syn)** cannot use the π bond from the back, but is still faster than 2. **1 > 3 > 2** → (b).

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