Topics in the November 2012 Exam Paper for CHEM1902

Click on the links for resources on each topic.

2012-N-2:

- Crystal Structures

2012-N-3:

- Weak Acids and Bases
- Calculations Involving pK_a

2012-N-4:

- Metal Complexes
- Coordination Chemistry

2012-N-5:

- Kinetics

2012-N-6:

- Intermolecular Forces and Phase Behaviour
- Physical States and Phase Diagrams

2012-N-7:

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- Alcohols
- Organic Halogen Compounds
- Aldehydes and Ketones
- Carboxylic Acids and Derivatives

2012-N-8:

- Amines
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2012-N-9:

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- Aromatic Compounds
- Organic Mechanisms and Molecular Orbitals

2012-N-12:

- Alcohols
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2012-N-13:

- Alcohols
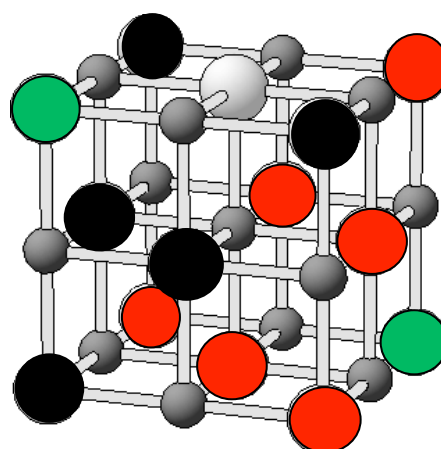- Carboxylic Acids and Derivatives
- Aromatic Compounds

- PdO is used as a hydrogenation catalyst and it crystallizes with the tetragonal structure shown below. NiO has a variety of uses and crystallizes with the rocksalt structure. The large spheres represent the oxygen atoms and the smaller spheres represent palladium or nickel atoms.
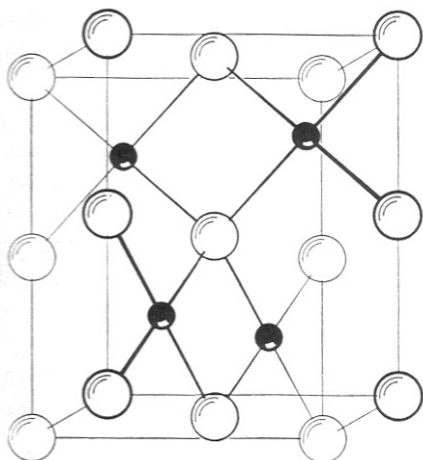
palladium(II) oxide, PdO   nickel(II) oxide, NiO

Show the structure on the left is consistent with the formula PdO.

In the unit cell there are:

      4 Pd atoms
      1 O atom in the centre
      2 × ½ = 1 O atom at the top and bottom faces
      4 × ¼ = 1 O atom at the equatorial edges
      8 × ⅛ = 1 O atom at the corners

This gives unit cell formula of Pd_4O_4 and thus empirical formula of PdO.

What is the coordination number about each metal atom?

Pd: **4**	Ni: **6**

The radius of the Pd^{2+} ion is 86 pm, that of the Ni^{2+} ion is 69 pm. Give a reason why the larger ion has a smaller coordination number.

Pd^{2+} (d^8) prefers square planar coordination and thus has a lower coordination number than Ni^{2+}. The ionic model would predict that the larger Pd^{2+} ion would have a higher coordination than Ni^{2+}. The preference of Pd^{2+} for square planar coordination overrides this.

Does either structure contain a close-packed arrangement of O^{2-} ions?

PdO: YES / **NO**	NiO: **YES** / NO

If YES, indicate the layers on the unit cell(s) above. **See coloured layers above**

**Marks
9**

- Boric acid, $B(OH)_3$, is a weak acid ($pK_a = 9.24$) that is used as a mild antiseptic and eye wash. Unusually, the Lewis acidity of the compound accounts for its Brønsted acidity. By using an appropriate chemical equation, show how this compound acts as a Brønsted acid in aqueous solution.

The boron atom in $B(OH)_3$ is electron deficient. It acts as a Lewis acid by readily accepting the lone pair from the oxygen in a water molecule to go from sp^2 to sp^3 hybridisation.
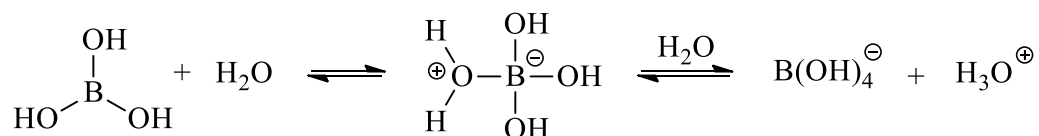
Solution A consists of a 0.050 M aqueous solution of boric acid at 25 °C. Calculate the pH of Solution A.

As boric is a weak acid, $[H_3O^+]$ must be calculated using a reaction table (acid = $B(OH)_3$ and base = $B(OH)_2^-$)

	acid	H_2O	$\rightleftharpoons$	H_3O^+	base
initial	0.050	large		0	0
change	-x	negligible		+x	+x
final	0.050 – x	large		x	x

The equilibrium constant K_a is given by: $K_a = \dfrac{[H_3O^+][\text{base}]}{[\text{acid}]} = \dfrac{x^2}{0.050-x}$

As $pK_a = -\log_{10}K_a$, $K_a = 10^{-9.24}$ and is very small, $0.050 - x \sim 0.050$ and hence:

$$x^2 = 0.050 \times 10^{-9.24} \qquad \text{or} \qquad x = 5.36 \times 10^{-6} \text{ M} = [H_3O^+]$$

Hence, the pH is given by:

$$pH = -\log_{10}[H_3O^+] = -\log_{10}(5.36 \times 10^{-6}) = 5.27$$

pH = **5.27**

At 25 °C, 1.00 L of Solution B consists of 10.18 g of $NaB(OH)_4$ dissolved in water. Calculate the pH of Solution B.

The molar mass of $NaB(OH)_3$ is:

**molar mass = [22.99 (Na) + 10.81 (B) + 4 (16.00 (O) + 1.008 (H))] g mol^{-1}
= 101.83 g mol^{-1}**

ANSWER CONTINUES ON THE NEXT PAGE

A mass of 10.18 g therefore corresponds to:

   number of moles = mass / molar mass = 10.18 g / (101.83 g mol^{-1}) = 0.100 mol

A 1.00 L solution contains this amount has a concentration of 0.100 M.

As it is a weak base, [OH$^-$] must be calculated by considering the equilibrium:

	base	H$_2$O	$\rightleftharpoons$	acid	OH$^-$
initial	0.100	large		0	0
change	-y	negligible		+y	+y
final	0.10 – y	large		y	y

The equilibrium constant K_b is given by:

$$K_b = \frac{[\text{acid}][\text{OH}^-]}{[\text{base}]} = \frac{y^2}{(0.100-y)}$$

For an acid and its conjugate base:

   pK_a + pK_b = 14.00

   pK_b = 14.00 – 9.24 = 4.76

As pK_b = 4.76, K_b = 10$^{-4.76}$. K_b is very small so 0.100 – y ~ 0.100 and hence:

   y^2 = 0.100 × 10$^{-4.76}$ or y = 0.00132 M = [OH$^-$]

Hence, the pOH is given by:

   pOH = -log$_{10}$[OH$^-$] = log$_{10}$[0.00132] = 2.88

Finally, pH + pOH = 14.00 so

   pH = 14.00 – 2.88 = 11.12

pH = **11.12**

Using both Solutions A and B, calculate the volumes (mL) required to prepare a 1.0 L solution with a pH = 8.50.

The ratio of acid to conjugate base needed can be calculated using the Henderson-Hasselbalch equation, pH = pK_a + log$\dfrac{[\text{base}]}{[\text{acid}]}$:

   8.50 = 9.24 + log$\dfrac{[\text{base}]}{[\text{acid}]}$ so $\dfrac{[\text{base}]}{[\text{acid}]}$ = 10$^{-0.74}$ = 0.182

ANSWER CONTINUES ON THE NEXT PAGE

A volume V_a of the acid and V_b of base are added together to give a solution with a total volume of 1.0 L so:

$V_a + V_b = 1.0$ L

Using $c_1V_1 = c_2V_2$, this mixing reduces the concentration of both:

acid: $(0.050$ M$) \times V_a = c_{acid} \times (1.0$ L$)$ so $V_a = 20. \times c_{acid}$
base: $(0.100$ M$) \times V_b = c_{base} \times (1.0$ L$)$ so $V_b = 10.0 \times c_{base}$

Using the concentration ratio from the Henderson-Hasselbalch equation above, the ratio of the volumes needed is therefore:

$V_b / V_a = (10.0 / 20.) \times c_{base} / c_{acid} = (10. / 20.) \times 0.182 = 0.0910$

or

$V_b = 0.0910 \times V_a$

From above, $V_a + V_b = 1.0$ L so:

$V_a + (0.0910 \times V_a) = 1.0$ L
$1.0091\ V_a = 1.0$ L
$V_a = 0.917$ L

Hence, $V_b = 0.083$ L.

- The red species $K_4[Mo_2Cl_8]$ is an historically important example of a metal-metal bonded complex. Use standard nomenclature to name the complex salt.

potassium octachloridodimolybdate(II)

$K_4[Mo_2Cl_8]$ possesses an extremely short Mo–Mo bond (214 pm), much shorter than the bonding distance between Mo atoms in Mo metal (273 pm)! Propose a reasonable explanation for the very short Mo–Mo bond length in the complex by adding *d*-electrons into the (partial) MO scheme shown below. Draw a structure for the complex that is consistent with the completed MO scheme and your explanation.
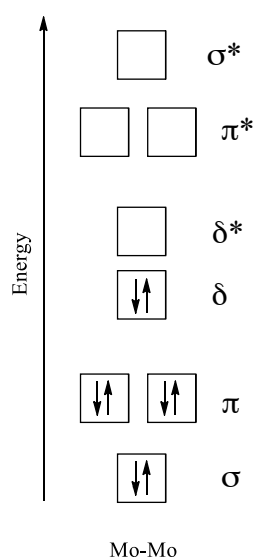
Mo^{2+} is d^4, so there are 8 *d* electrons which all occupy the σ, π and δ bonding orbitals as shown.

With 8 bonding electrons and no anti-bonding electrons, the complex therefore has a bond order of 4 and consequently a very short bond length.
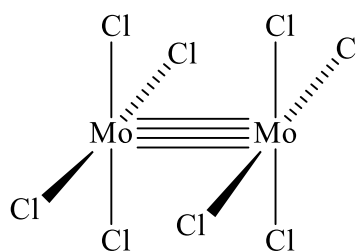
Oxidation of the complex by one electron gives rise to a paramagnetic species in which the Mo-Mo distance increases significantly. Propose a reasonable hypothesis for the bond lengthening phenomenon.

Oxidation is the loss of 1 electron which is removed from the highest occupied molecular orbital: the δ bonding orbital. As this leads to an unpaired electron in this orbital, it is paramagnetic species.

The number of bonding electrons is thus reduced to 7. This reduces the bond order from 4.0 to 3.5, thus weakening and lengthening the Mo–Mo bond.

- Four experiments were conducted to discover how the initial rate of consumption of BrO_3^- ions in the reaction below varied as the concentrations of the reactants were changed.

$$BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2 + 3H_2O$$

Experiment	Initial concentration (mol L^{-1})			Initial rate (mol L^{-1} s^{-1})
	BrO_3^-	Br^-	H^+	
1	0.10	0.10	0.10	1.2×10^{-3}
2	0.20	0.10	0.10	2.4×10^{-3}
3	0.10	0.30	0.10	3.5×10^{-3}
4	0.20	0.10	0.15	5.4×10^{-3}

Use the experimental data in the table above to determine the order of the reaction with respect to *each* reactant.

Between experiments (1) and (3), [Br⁻] and [H⁺] are kept constant but [BrO₃⁻] is doubled. This doubles the rate: the rate is proportional to [BrO₃⁻]^1 and so is first order with respect to BrO₃⁻.

Between experiments (2) and (4), [BrO₃⁻] and [Br⁻] are kept constant but [H⁺] is increased by a factor of (0.15/0.10) = 1.5. This increases the rate by a factor of (5.4 × 10⁻³ / 2.4 × 10⁻³) = 2.25: the rate is proportional to [H⁺]^2 as (1.5)^2 = 2.25 and so is second order with respect to H⁺.

Between experiments (1) and (2), [BrO₃⁻] and [H⁺] are kept constant but [Br⁻] is increased by a factor of 3. This increases the rate by a factor of (3.5 × 10⁻³ / 1.2 × 10⁻³) = 2.9: the rate is proportional to [Br⁻]^1 and so is first order with respect to Br⁻.

Overall,

   rate = k[BrO₃⁻][Br⁻][H⁺]^2

What is the rate of formation of Br_2 when $[BrO_3^-] = [Br^-] = [H^+] = 0.10$ M?

From the table, when [BrO₃⁻] = [Br⁻] = [H⁺] = 0.10 M, the rate of consumption of BrO₃⁻ is 1.2 × 10⁻³ M s⁻¹. From the chemical equation, Br₂ is produced at three times this rate.

The rate of production of Br₂ is 3.6 × 10⁻³ M s⁻¹.

Write the rate law for the reaction and determine the value of the rate constant, k.

From above, rate = k[BrO₃⁻][Br⁻][H⁺]^2. Using experiment (1):

ANSWER CONTINUES ON THE NEXT PAGE

rate = $k[BrO_3^-][Br^-][H^+]^2$
     = $k(0.10 \text{ M})(0.10 \text{ M})(0.10 \text{ M})^2 = k(0.00010 \text{ M}^4) = 1.2 \times 10^{-3} \text{ M s}^{-1}$

So,

k = $(1.2 \times 10^{-3} \text{ M s}^{-1}) / (0.00010 \text{ M}^3) = 12 \text{ M}^{-3} \text{ s}^{-1}$

- The diagram below shows a simplified phase diagram of helium.
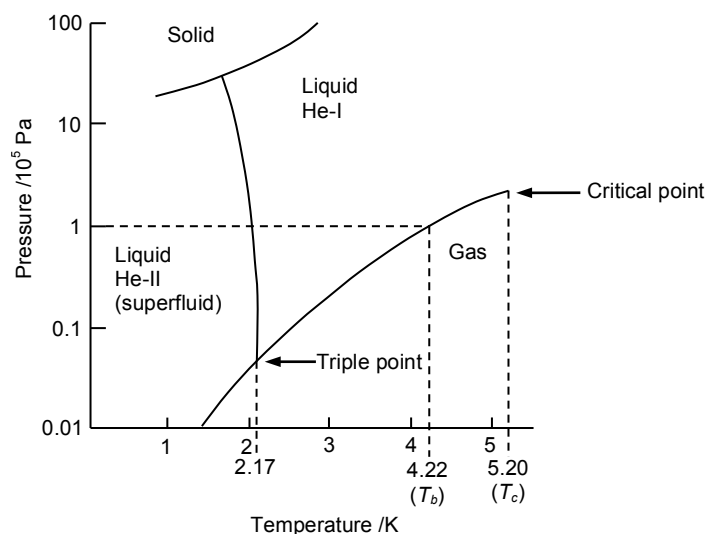
Describe two unusual properties of helium (other than the "superfluid" He-II phase) that are *not* shared by most substances.

The unusual properties of helium that can be deduced from the phase diagram include:

   (i)   It has 2 triple points.
   (ii)   There is no gas/solid equilibrium line (*i.e.* helium does not sublime).
   (iii) There is a liquid/liquid equilibrium line.
   (iv)   The triple points involve 2 liquid phases.
   (v)   helium cannot exist as a solid at atmospheric pressure.

Is it possible to liquefy helium above 5.20 K? Explain your answer.

No. If $T > 5.2$ K, helium exists as a supercritical fluid above ~2×10^5 Pa and as a gas below this pressure.

Why is the liquefaction of He very difficult, even at low temperatures?

Intermolecular forces between He atoms are extremely weak.
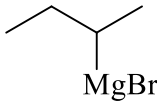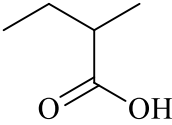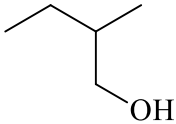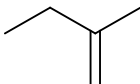
The electrons are held very tightly in the small 1s orbital. The atom is therefore very small and the electron cloud is not very polarisable. As a result, the interatomic dispersion forces required for liquefaction are very weak and they can only sufficient to keep He atoms in a liquid phase at temperatures approaching absolute zero.

**Marks
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- Consider the following reaction sequence beginning with the alkene **A**.
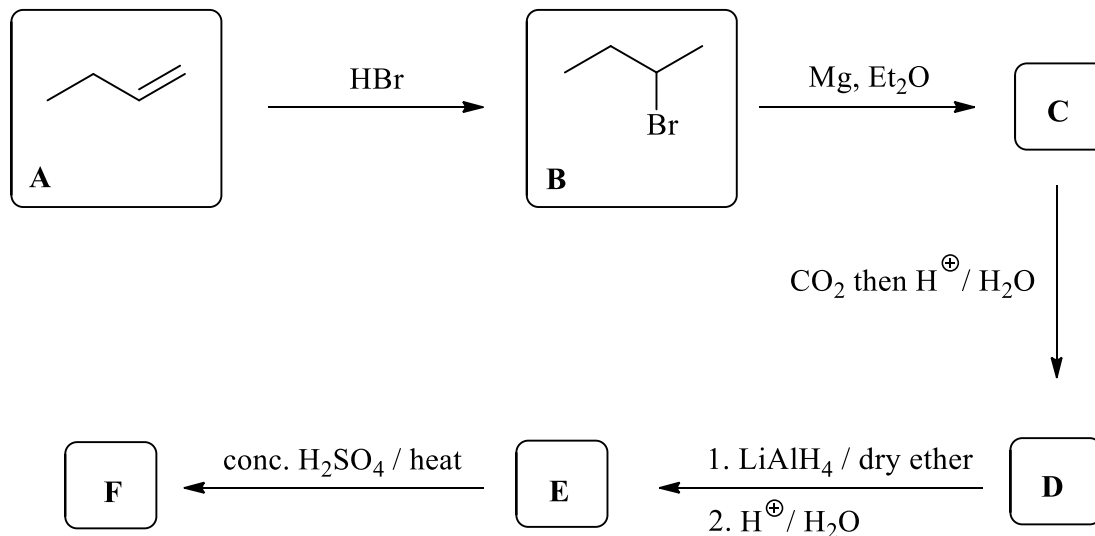
Suggest structures for compounds **C – F** in the reaction sequence above.

C	D
E	F

Describe the selectivity observed, and briefly explain the reasons for it, in the conversion of alkene **A** to compound **B**.

Markovnikov's rule: the H$^+$ of HBr adds to C1 leading to a secondary carbocation rather than to C2 which leads to a primary carbocation. The more substituted carbocation is more stable due to hyperconjugation.

- Consider the three nitrogen-containing compounds **P**, **Q** and **R**.

P	**Q**	**R**
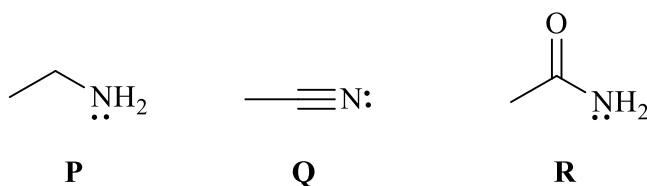
What is the hybridisation at *N* in compound **P**?	*sp*^{3}
What is the hybridisation at *N* in compound **Q**?	*sp*

Use this information to decide which of **P** or **Q** is more basic. Explain your reasoning.

P is more basic. The s*p*^{3} hybridised N has more *p* orbital character (75%) compared to s*p* (50%). P therefore has a more diffuse lone pair that is more available for protonation. Conversely, the lone pair in Q is more tightly bound and Q is therefore a weaker base.

Show curly arrows and another structure to show how compound **R** is stabilised by resonance.
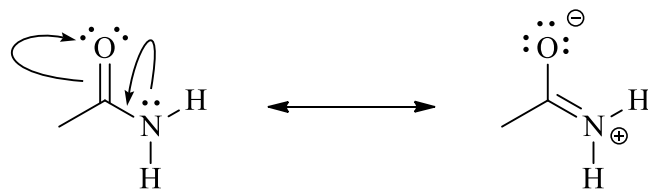
Which is more basic, compound **P** or compound **R**? Why?

P is more basic.

The 'lone pair' in R contributes to the resonance structure and is partially delocalised into the carbonyl group and is therefore unavailable for protonation.

• Consider the structure of dihydrocarvone shown below.
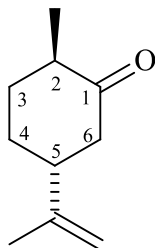
Assign the absolute configuration of dihydrocarvone. Explain your reasoning.
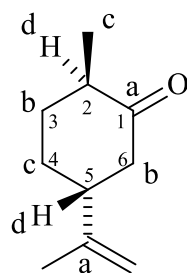
C_2: (R)
Around C_2, the order of priorities is:
   a: C_1(O,O,C) > b: C_3(C,H,H) > c: C_{methyl}(H,H,H) > d: H

Looking down C_2–H bond, a →b→c is clockwise

C_5: (R)
Around C_5, the order of priorities is:
   a: C(C,C,C) > b: C_6(C,H,H) > c: C_4(C,H,H) > d: H

As C_4 and C_6 are equivalent, C_1 > C_3 is used to prioritise them.
Looking down C_5–H bond (*i.e.* out of paper), a →b→c is clockwise

Draw all of the products that can result from the electrophilic addition of HBr to dihydrocarvone and explain the isomeric relationship between each pair.
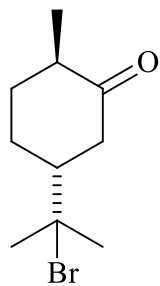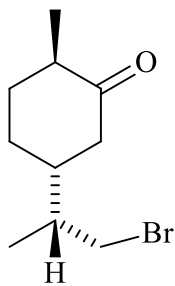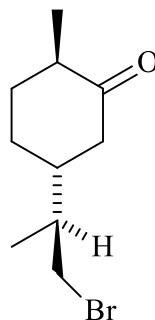
A   B   C

A and B are constitutional isomers. A and C are constitutional isomers. B and C are diastereoisomers.

- Apply your understanding of curly arrows to complete a mechanism for the following S_N reaction:
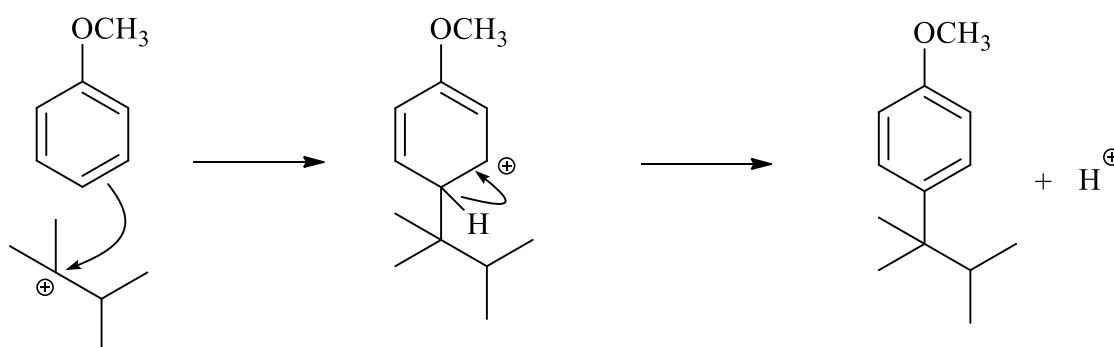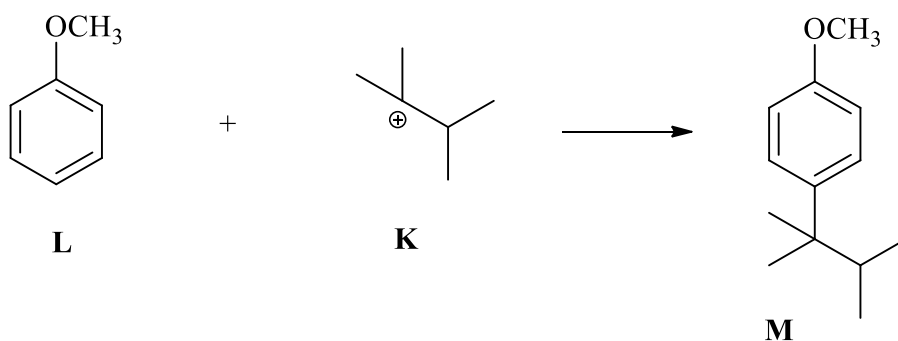
Marks

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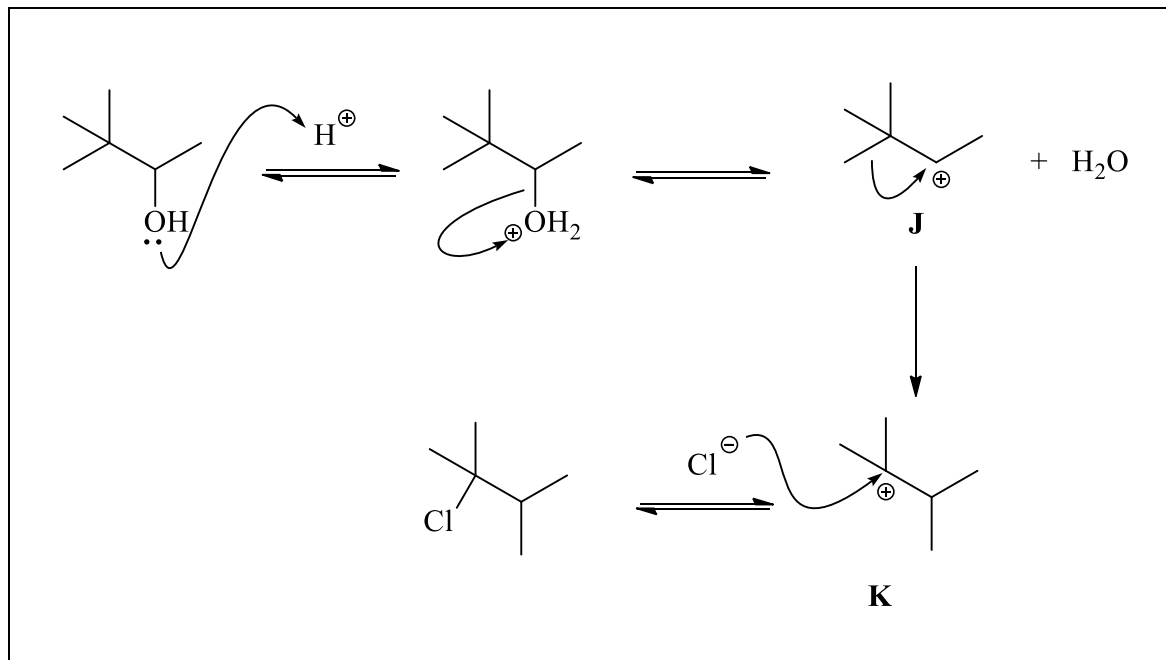
Why does the rearrangement step (**J** → **K**) occur?

K (the tertiary carbocation) is more stable than **J** (the secondary carbocation) as it is more substituted and hence more stabilised by hyperconjugation.

Reaction of **K** with anisole (methoxybenzene, **L**) gives **M** as the major product. Propose a mechanism for this transformation.

L   +   **K**   →   **M**

+ H$^{\oplus}$

Briefly explain why the 4-substituted product **M** is formed preferentially.

Substitution at positions 2 and 4 is favoured over position 3 due to the relative stabilities of the Wheland intermediates. There are 4 resonance contributors for substitution at positions 4 (or 2), but only 3 for substitution at position 3. Position 4 is favoured over position 2 due to steric effects - the methoxy group attached to C1 physically blocks approach of the attacking carbocation./
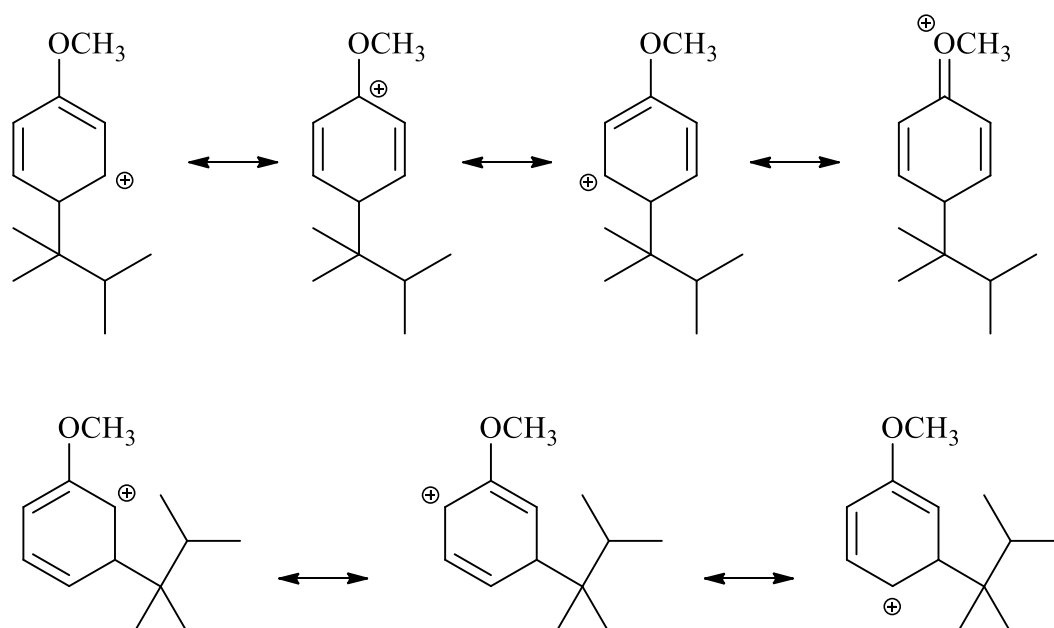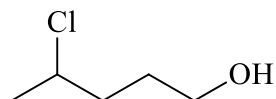
- Propose a mechanism for the following reaction.

T
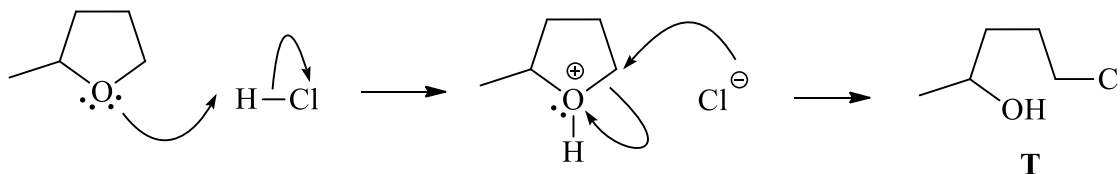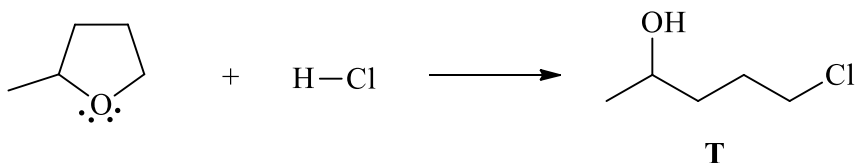
What isomeric product might also form in this reaction?

If the Cl⁻ attacks on the left hand side of the molecule, the analogous reaction leads to:
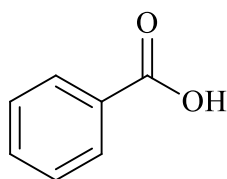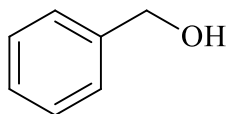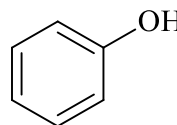

Why is **T** the major product?

Steric effects. The CH₂ group on the right is more accessible than the CH(CH₃) group on the left for S$_N$2 attack by the Cl⁻ nucleophile.

- Benzoic acid **H**, benzyl alcohol **I** and phenol **J** are shown below. The pK_a values of these three compounds are 15.2, 9.9 and 4.2, but not in that order.

| | **H** | **I** | **J** |

Assign the correct pK_a to each of these three compounds.
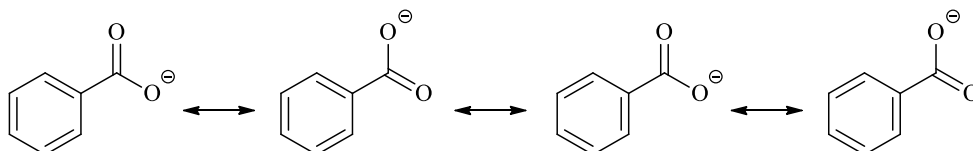
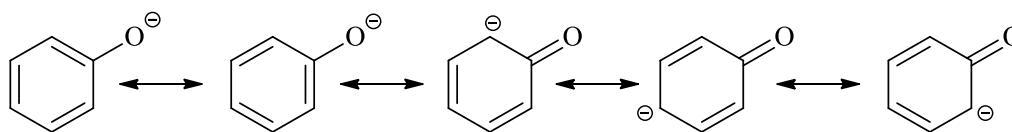| pK_a values: | **H = 4.2** | **I = 15.2** | **J = 9.9** |

Draw resonance structures to explain your answer.

The conjugate base of H is stabilised by delocalisation of the negative charge over two electronegative O atoms and over the ring:


The conjugate base of J is stabilised by delocalisation of the negative charge over an O atom and the ring:

As the delocalisation places negative charge over C as well as O, the stabilisation is smaller than for H.

By resonance stabilisation is possible for the conjugate base of I.

Would you expect 4-nitrophenol, **K**, to be more or less acidic than phenol, **J**? Explain your answer.
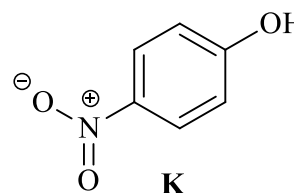
K will be more acidic than J as the negative charge of the phenoxide ion can be delocalised into the nitro group, increasing the resonance stabilisation.

etc.