2023 Y6 H3 Chemistry Preliminary Exams – Suggested Solutions

- **1(a)** It refers to the balance between <u>high energy content</u> with <u>low sensitivities/good</u> <u>thermal stability (safety)/OWTTE</u>.
- **1(b)** The integration approach relies on the <u>known properties of different types of</u> <u>structures/moiety</u>, thus <u>combining the advantages of each moiety</u> in the design of the compound (OWTTE).

Or

The integration approach may accelerate the development of advanced EMs instead of developing a molecule from scratch.

1(c)(i) AEMs need to have high energy content so that large amounts of energy can be released when detonated.



- $\Delta H_{f}^{\Theta} = [2 \Delta H_{atom}^{\Theta} \text{ of } C + BE(N \equiv N) + BE(H H) + \frac{1}{2}BE(O=O)] [BE(C C) + 2 BE(C H) + 2 BE(N O) + 2 BE(C=N)]$ = [(2x715) + 944 + 436 + $\frac{1}{2}(496)$] - [350 + (2x410) + (2x201) + (2x610)] = $\frac{+266 \text{ kJ mol}^{-1}}{2}$
- **1(c)(iii)** Standard enthalpy change of vaporisation of (liquid) 1,2,5-oxadiazole.
- **1(d)** Tricyclic structure in compound **A** provides <u>larger π -conjugated systems</u> which increases the stability of the molecule.



1(f)(i) Condensation / addition-elimination



1(f)(iii) (CH₃CO)₂O acts as a <u>Lewis acid</u> as it <u>accepts an electron pair from HNO₃ leading to</u> the formation of acetyl nitrate.

 H_2SO_4 acts as a <u>Bronsted-Lowry acid</u> as it <u>protonates HNO_3</u> leading to the formation of the NO_2^+ electrophile.

2(a)(i)

- Amide **J** is less basic than amine **H** due to the <u>delocalisation of the lone pair of</u> <u>electrons on the N atom into the C=O</u>. Hence, the lone pair is <u>not available</u> to accept a proton.
 - Amidine K is more basic than amine H as the delocalisation of the nitrogen lone pair in the NH₂ group increases the electron density on the NH group. Accept "positive charge on conjugate acid is delocalised over both N atoms, stabilising the conjugate acid".

- **2(a)(ii)** L is more basic than K as the additional NH can donate electron density onto the underlined NH, increasing electron density on the underlined N atoms.
- 2(a)(iii) The reaction of K is slower.

The amide carbon in \mathbf{J} is <u>more electron deficient</u> than the amidine carbon in \mathbf{K} as <u>oxygen is more electronegative than nitrogen</u>, and is hence more susceptible towards nucleophilic attack.

2(a)(iv) The C=O bond in **J** absorbs at higher frequency than C=N bond in **K** as the <u>C=O</u> bond is stronger (740 kJ mol⁻¹) than the C=N bond (610 kJ mol⁻¹).

Can accept explanation based on lower atomic mass of N leading to higher frequency of C=N

2(b)(i) Since the <u>electronegative iodine atom is closer to the negatively-charged C</u> atom in CH₃COCHI⁻ than that in ⁻CH₂COCHI and is able to <u>disperse the negative charge to a</u> <u>larger extent</u>, the <u>CH₃COCHI⁻ intermediate is more stable/ lower in energy</u> and formed faster.



- 2(b)(iii) Using the same concentrations and volumes of iodine, NaOH and the ketones,
 - Pour iodine and NaOH in a conical flask. Place the flask over a mark.
 - Add in ketone and start stopwatch immediately.
 - Stop stopwatch once the yellow ppt obscures the mark completely / time taken for first appearance of yellow ppt.
- 2(b)(iv) The kinetic product Q is favoured when a <u>bulky base</u> like LDA is used. There is <u>less</u>
 (1) <u>steric hindrance on a primary α-carbon atom</u> compared to a secondary α-carbon atom, hence less E_a is required to form the kinetic intermediate, which is formed faster.

2(b)(iv) A shorter reaction time favours the kinetic product which is formed faster and does

(2) <u>not allow time for the thermodynamic product to be formed</u> to an appreciable extent.

AND

A <u>low temperature</u> favours the kinetic product as it <u>does not allow the kinetic product</u> to overcome the E_a barrier to form the thermodynamic product Or

Low temperature reduces the <u>proportion of reactant molecules that can overcome the</u> <u>activation energy required to form the thermodynamic product</u> J.

2(c) CHI₃ has one molecular ion peak at m/z = 394 corresponding to [CH¹²⁷I₃]⁺.

•				
species	[CH ³⁵ C <i>l</i> ₃]⁺	[CH ³⁵ Cl ₂ ³⁷ Cl] ⁺	[CH ³⁵ Cl ³⁷ Cl ₂] ⁺	[CH ³⁷ C <i>l</i> ₃]⁺
m/z	118	120	122	124
relative abundance	$\left(\frac{3}{4}\right)^3 = \frac{27}{64}$	$3\left(\frac{3}{4}\right)^2\left(\frac{1}{4}\right) = \frac{27}{64}$	$3\left(\frac{3}{4}\right)\left(\frac{1}{4}\right)^2 = \frac{9}{64}$	$\left(\frac{1}{4}\right)^3 = \frac{1}{64}$
	27 :			1
		27 :	9 :	

CHCl₃ has four molecular ion peaks:

3(a)



2 electrons in one sp² orbital, 1 electron in each of remaining orbitals

3(b)(i) The <u>electron density of the pyridine ring is decreased</u> by the <u>electron-withdrawing</u> effect of the electronegative nitrogen atom.



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Attack at the C4 position results in the <u>positive charge on the electronegative</u> <u>N atom</u>, giving rise to a <u>very unstable</u> canonical form. Hence, substitution at C4 occurs less readily.



- **3(c)(ii)** Compound **U**: 2 doublets and 2 doublet of doublets Compound **S**: 2 doublets
- **3(d)(i)** The cationic intermediate formed with pyridine reacts faster with alcohol as the partial positive charge on the acyl carbon is intensified by the electron-withdrawing positively charged nitrogen atom.
- **3(d)(ii)** Pyridine is protonated in the course of the reaction and is consumed by the acid-base reaction.



4(a)

TMS is commonly used as a standard as

- It gives an <u>intense sharp signal</u> even at low concentrations since it has <u>12</u> <u>chemically equivalent protons</u>.
- It is soluble in most organic solvents.
- It is <u>chemically inert</u> and has a <u>low boiling point (26.5 °C)</u> so that it is <u>easily</u> <u>removed</u> from a recoverable sample of a valuable organic compound.
- It <u>resonates at a frequency lower than that of any ¹H nuclei</u> in common organic molecules and so its peak <u>does not interfere</u> with the other peaks.
- **4(b) W** has ¹H NMR peaks present at <u>6.8 and 7.5 ppm which represent aromatic protons</u>, while **V** does not. The <u>higher degree of conjugation</u> in **W** will cause the <u>energy gap</u> of $\pi \rightarrow \pi^*$ to decrease, shifting the UV absorption to a longer wavelength. Therefore, **W** will have a greater λ_{max} than **V**.

4(c) IR Analysis

absorption / cm ⁻¹	Functional group
1640 – 1750 absent	No C=O stretch, no ketones
3030	C=C stretch, alkene present
3360 (w)	N-H stretch, amine present

¹H NMR Analysis

chemical shift / ppm	no. of H	multiplicity	deductions
4.8	1	singlet	NH proton
3.9	2	triplet	Two separate –CH groups (H_b) with neighbouring –CH ₂ group (H_a) H_b shows higher chemical shift than H_a due to closer proximity to the electronegative N atom.
3.2	2	triplet	$-CH_2$ group (H _a) with two neighbouring $-CH$ (H _b) groups with chemically equivalent protons.
2.0	6	singlet	2 isolated –CH $_3$ groups (H _c)
6.8 and 7.5 for W	-	-	Aromatic protons (V could be cyclized from 1,5-diketone and NH ₃)
а			



4(d) At 280nm, 0.86 = 12000[V](1.0) + 5600[W](1.0) --- equation (1)At 300nm, <math>0.41 = 3400[V](1.0) + 14200[W](1.0) --- equation (2)From eqn(1), [V] = <math>(0.86 - 5600[W]) / 12000substitute into eqn (2) 0.41 = 3400((0.86 - 5600[W]) / 12000) + 14200[W]0.41 = 0.2833(0.86 - 5600[W]) + 14200[W]0.41 = 0.2436 - 1586.48[W] + 14200[W]0.41 = 0.2436 - 1586.48[W] + 14200[W] $[W] = 1.319 \times 10^{-5} \text{ mol dm}^{-3}$ Sub in eqn (1) $0.86 = 12000[V] + 5600(1.319 \times 10^{-5})$ 0.86 = 12000[V] + 0.073876 $[V] = 6.551 \times 10^{-5} \text{ mol dm}^{-3}$

:: $[V] = 6.55 \times 10^{-5} \text{ mol dm}^{-3}, [W] = 1.32 \times 10^{-5} \text{ mol dm}^{-3} (3 \text{ s.f.})$

5(a) H_a is acidic as the negative charge on the carbanion formed after deprotonation can be delocalised into the C=O via resonance.



- **5(b)(i)** As compound **C** is a tertiary bromoalkane, there is too much steric hindrance for $S_N 2$ reaction.
- **5(b)(ii)** As the carbocation formed from compound **C** is connected to two other <u>electron</u> <u>withdrawing groups</u> (CN and COOR), the <u>positive charge of the carbocation is</u> <u>intensified</u>, which makes the intermediate unstable.



5(c)(i) % ee = % major enantiomer – % minor enantiomer

Let % major enantiomer = x % 97 = x - (100 - x)x = 98.5 % Ratio of <u>98.5 : 1.5</u>

5(c)(ii) Both chiral carbons have the R configuration.

5(c)(iii) The <u>activation energy for pathway B is lower</u> since the transition state of pathway B is lower in energy. Hence, the product formed from pathway B will be the major product.



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5(d)(ii) Since the neighbouring group participation speeds up the reaction, an antiperiplanar / trans-diaxial (check) configuration is required. *trans*-2-iodocyclohexyl brosylate is able to undergo ring-flip to get an antiperiplanar configuration between -I and -OBs.



5(d)(iii) Use a <u>bulky base</u> such as potassium tert-butoxide.



- **5(d)(v)** If the product is the substitution product, a strong C=O absorption peak will be observed in the region of 1710 1750 cm⁻¹. If the product is the elimination product, a C=C absorption peak will be observed in the region of 1635 1690 cm⁻¹.
- 6(a) <u>Strong N=N triple bonds</u> formed leading to an <u>energetically favourable reaction / ΔH ≤ 0 Formation of <u>gaseous</u> N₂ increases <u>entropy of the system / $\Delta S > 0$ </u></u>
- **6(b)** The aryl carbocation is less stable as the positive charge in the empty sp² orbital is not stabilised, whereas the positive charge in the empty p orbital of an alkyl carbocation is stabilised by adjacent electron-donating alkyl groups.



 $6(c)(ii) \quad RNH_2 + NO^+ \rightarrow RN_2^+ + H_2O$



6(d)(ii)(The resulting protonated species is more effectively stabilised by resonance by the
 1) N,N-dimethylphenylamine group which is more electron rich than the benzenesulfonate group.



Alternative: electron donating effect of $-N(CH_3)_2$ via resonance which places a negative charge on N_a in one of its canonical forms

- 6(d)(ii)(The <u>red form</u> is more highly conjugated because it <u>absorbs a frequency of light at a</u> longer wavelength / lower frequency (green) than the yellow form (which absorbs violet).
- 6(e)(i) 1 and 2a occur at -40 °C and 2b occurs at 0 °C.

Possible reasons:

- At -40 °C, not all the N₂ is formed. This means that there is more than one reaction occurring at that temperature.
- The intermediate formed in the competing reaction is stable at -40 °C but breaks down at 0 °C to form the remaining N₂.
- If only route 1 / only route 2 occurred at -40 °C, then all the N₂ would have been formed.
- If only route 2a occurred at -40 °C, then there would be no N₂ formation at -40 °C.
- **6(e)(ii)** $t_{1/2}$ is constant at 4.5 min from 0% to 38% N₂ formation and 38% to 57% N₂ formation, therefore the direct route is overall 1st order.
- **6(e)(iii)** The S_N1 reaction would have produced 100% labelled ${}^{15}N-{}^{14}N$ molecules, which was not observed.



(Other possible intermediates, or a concerted mechanism can be accepted as long as it is consistent with product composition.)

Since phenylpentazole has a symmetrical 5-membered ring, it can give rise to an equimolar mixture of the two benzenediazoazide species shown. These molecules then break down to give an equimolar mixture of the $^{15}\rm N$ labelled and unlabeled N_2 molecules.

7(a)(i) top face: more steric hindrance



bottom face: less steric hindrance

As the <u>top face of catalyst **M** is more sterically hindered</u>, it will be more favourable for the <u>methyl group of **D** to face downwards</u> as it bonds with catalyst **M** and BH₃. Hence, the <u>hydrogen atom (from BH₃) will be added to the carbonyl carbon</u> of **D** from <u>out of</u> the plane direction, resulting in the major product shown.

- 7(a)(ii) KMnO₄(aq), NaOH(aq), cold (mild oxidation to form 1,2-diol)
- **7(a)(iii)** The TBDMS group acts as a protecting group for the alcohol (formed in step 1). This prevents the alcohol group from being oxidised in step 3 / forming acetal in step 4.
- 7(a)(iv)

7(b)(i)



The groups attached to each sp² C (C1 and C2) on the trisubstituted double bond are

assigned priority in order of decreasing atomic number.

C1 : C in ring has higher atomic number and hence higher priority over H.

C2 : O in ring has higher atomic number and hence higher priority over C.

Since the two lowest priority groups are on the <u>same side</u> of the C=C bond, it is of a <u>*Z* configuration</u>.





(peaks h to I are for reference only)

7(b)(iv) Structure of F:



Information	Deduction
F and harziphilone are constitutional	Molecular formula of F is $C_{15}H_{18}O_4$.
isomers.	
For F , peak g shifted to a higher	-CH ₂ -O protons in harziphilone are
chemical shift of 5.90 ppm to 5.92 ppm.	converted to <u>alkenyl protons</u> in F .
λ_{max} of F is smaller than that of	F has smaller extent of conjugation
harziphilone.	compared to harziphilone.



- 7(c)(ii) As seen from (c)(i), the <u>HOMO of G interacts with the LUMO of chloroethene / ethene</u> during the Diels-Alder reaction. Since the <u>HOMO-LUMO gap between G and</u> <u>chloroethene is smaller</u> than that between G and ethene, the Diels-Alder reaction is therefore faster.
- 7(c)(iii) resonance structures:



Due to the <u>resonance electron-donating effect of $-NH_2$ group in **H**, the terminal carbon nearer to the $-NH_2$ group is <u>more electron rich</u>. Also, the <u>resonance electron-withdrawing effect of -CN group</u> in **J** causes the terminal carbon in **J** to be <u>more electron deficient</u>.</u>

Hence, in the concerted Diels-Alder reaction between **H** and **J**, the <u>electron flow from</u> the more electron rich terminal carbon in **H** to the more electron deficient carbon in **J** is preferred, forming **K** as the major product.

