2013 JC2 H2 Chemistry Preliminary Examination Paper 3 Suggested Answers

1 **(a)** **(i)** $Pb(s) + 4HNO_3(aq) \rightarrow Pb(NO_3)_2(aq) + 2NO_2(g) + 2H_2O(l)$

(ii) Al^{3+} left in solution **X** exists as $Al(H_2O)_6^{3+}$.

Due to high charge density of Al^{3+}, it hydrolyses in water to give a weakly acidic solution. Al^{3+} polarises the electron cloud of H_2O molecule attached to it which will weaken and break its O–H bond, releasing H^+.

$$Al(H_2O)_6^{3+} \rightleftharpoons Al(H_2O)_5(OH)^{2+} + H^+$$

(iii) Since $Al_2(SO_4)_3 \equiv 2Al(H_2O)_6^{3+}$,

$$[Al(H_2O)_6^{3+}] \text{ in solution } \mathbf{X} = 2 \times \frac{60}{60+40} \times 0.100 = 0.\ 120 \text{ mol dm}^{-3}$$

$$[H^+] = \sqrt{c_{acid} ? K_a} = \sqrt{0.120 \times 1.4 \times 10^{-5}}$$

$$= 1.30 \times 10^{-3} \text{ mol dm}^{-3}$$

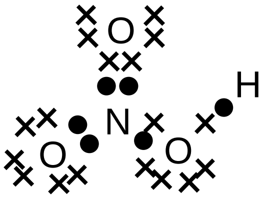
(b) **(i)** $\Delta H_f(NO_2(g)) = 0.5\ [(+183) + (-116)] = +33.5 \text{ kJ mol}^{-1}$

(ii)

$$\begin{tikzcd}
3NO_2(g) + H_2O(l) \arrow[r, "\Delta H_r"] & 2HNO_3(aq) + & NO(g) \\
& \frac{3}{2}N_2(g) + 3O_2(g) + H_2O(l) \arrow[ul, "3(+33.5)"] \arrow[u, "\frac{1}{2}(-256)"'] \arrow[ur, "\frac{1}{2}(+183)"'] &
\end{tikzcd}$$

$$\Delta H_r = -3(+33.5) + \frac{1}{2}(-256) + \frac{1}{2}(+183) = -137 \text{ kJ mol}^{-1}$$

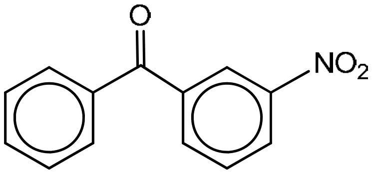
(c) **(i)**



(ii) HNO_3 can accept H^+ due to the availability of the lone pair of electrons on O atom of –OH group. After accepting H^+ from H_2SO_4, the unstable $H_2NO_3^+$ intermediate formed quickly breaks down to NO_2^+ and H_2O.

1 **(d)**

A:



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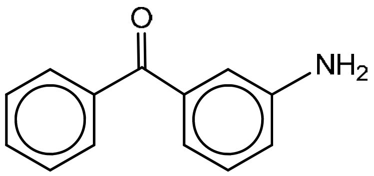
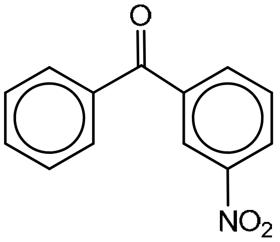


OR

A:



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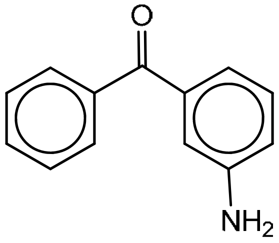
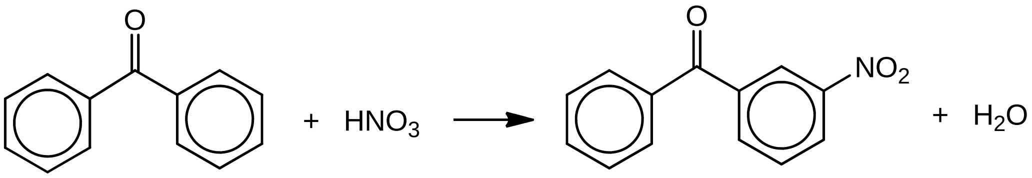




Sn, conc HC*l*, heat under reflux, followed by NaOH(aq)

(e) **(i)** A *weak* acid dissociates partially in water.

$HCN = H^+ + CN^-$

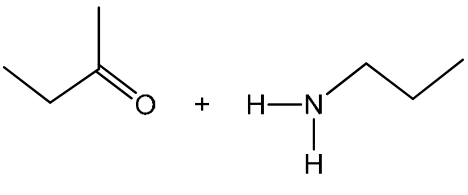
(ii) At high $[H^+]$,
equilibrium position of $HCN = H^+ + CN^-$ shifts left, resulting in low $[CN^-]$ which slows down step 1.

At low $[H^+]$,
equilibrium position of $HCN = H^+ + CN^-$ shifts right, resulting in low [HCN] which slows down step 2.

(iii) I: condensation

II: reduction

(iv)



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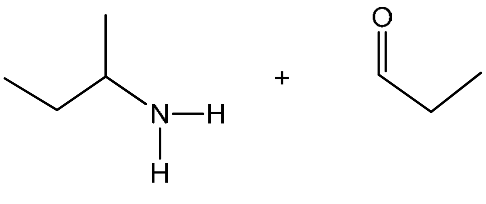


2 **(a)** **(i)** Since O^{2-} has a smaller radius, it is less polarisable than Cl^{-}. Hence, Fe_2O_3 is more thermally stable/ decomposes at a higher temperature.

(ii) Fe_2O_3 has giant ionic structure while $FeCl_3$ has simple covalent structure.

Much larger amount of energy is required to overcome the strong ionic bonds between Fe^{3+} and O^{2-} as compared to that required to overcome the weak van der Waals' forces between $FeCl_3$ molecules.

(b) **(i)** **D**: CuC*l*

E: $Cu(H_2O)_6^{2+}$

(ii) Cu(I) in D has a d^{10} configuration/ completely filled d–orbitals and hence, electron transition between d–orbitals is not possible. Thus, CuC*l* is white in colour.

Cu(II) in E has a d^9 configuration/ partially filled d–orbital and hence, electrons transition between d–orbitals is possible.

In Cu(II) complex ion, the presence of ligands causes the five 3d orbitals to split into 2 sets of different energies.

The difference in energies between the 2 sets of 3d orbitals is relatively small such that radiation from the visible region region of the electromagnetic spectrum when an electron moves from a d–orbital of lower energy to another partially–filled d–orbital of higher energy.

Hence, the Cu(II) compounds are coloured and the colour observed is the complement of the colours absorbed.

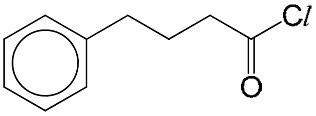
(c) **(i)** Electrophilic substitution

(ii) Step 3: acidified $K_2Cr_2O_7$(aq), heat under reflux

Step 4: PCl_5(s) *OR* PCl_3, heat *OR* $SOCl_2$, heat

OR PBr_3, heat *OR* $SOBr_2$, heat

(iii)



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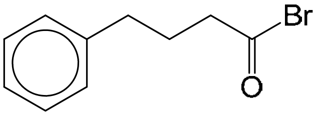


structure to correspond to reagent given in step 4

(iv) *E*(C–I) = + 240 kJ mol^{-1} *E*(C–C*l*) = + 340 kJ mol^{-1}

Since *E*(C-I) is smaller than *E*(C–C*l*) and thus C–I bond is weaker than the C–C*l* bond, it is easier to break C–I bond. Hence, **F** should contain the C*l* atom, rather than I atom.

OR

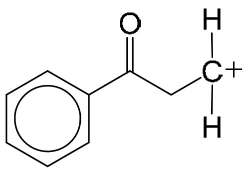
(Atomic) radius of I = 0.133 nm; (Atomic) radius of C*l* = 0.099 nm

Due to larger I atom, C–I bond is longer and weaker than the C–C*l* bond, it is easier to break C–I bond. Hence, **F** should contain the C*l* atom, rather than I atom.

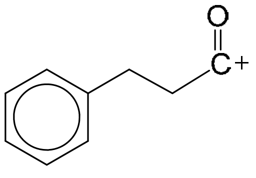
(v) Test : (1) Add NaOH(aq) to a sample of F and heat.
(2) Acidify the mixture with HNO_3(aq) to remove excess NaOH.
(3) To the resulting mixture, add $AgNO_3$(aq).

Observation: If the student's suggestion is not correct, white ppt of AgC*l* will be formed instead of yellow ppt of AgI.

2 (c) (vi) The electron–withdrawing C=O in **H** is directly bonded to benzene ring, making the benzene ring less electron–rich and thus less susceptible towards electrophilic attack.



electrophile from **H**



electrophile from **J**

Since C+ from **J** is directly attached to an electronegative O atom, it is highly electron deficient and thus a stronger electrophile than C+ from **H**.

Hence, **H** would require a harsher condition such as higher temperature or longer period of heating for Friedal–Crafts reaction to occur, as compared to **J**.

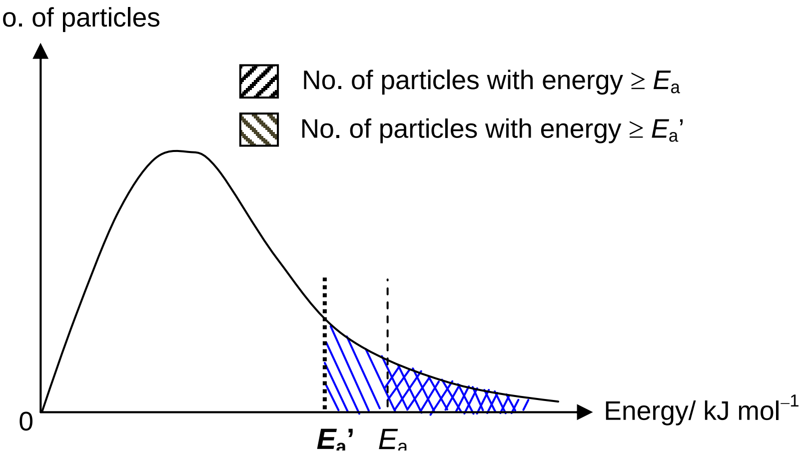
3 (a) (i) –1

(ii) $CH_3CH_2OH(aq) + O_2(g) \rightarrow CH_3COOH(aq) + H_2O(l)$

(iii) When $[CH_3CH_2OH]$ increases, the equilibrium position of $CH_3COOH + 4e^- + 4H^+ \rightleftharpoons CH_3CH_2OH + H_2O$ shifts left so as to react away some CH_3CH_2OH, causing $E(CH_3COOH/CH_3CH_2OH)$ to become more negative.

Hence, the voltage of the breathalyser will become more positive.

(b)



Silver nitrate catalyst provides an alternative reaction path of lower activation energy (E_a’) than that of the uncatalysed reaction. Thus, more particles have the minimum energy required to react. Therefore, the frequency of effective collisions between particles with energy ≥ E_a’ increases and hence, the reaction rate increases (i.e. test result is obtained within a short period of time).

(ii) **K**: $K_3Cr(OH)_6$ *OR* $Cr(OH)_6^{3-}$

L: K_2CrO_4 *OR* CrO_4^{2-}

(iii) $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons Cr^{3+} + 7H_2O \quad E^\ominus = +1.33\ V$

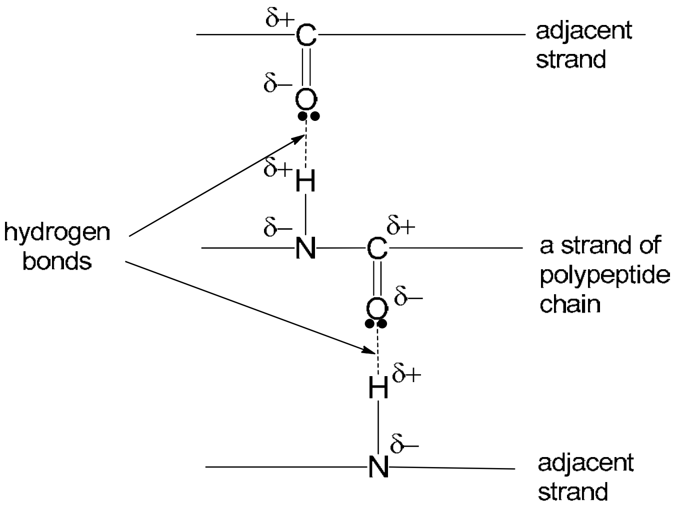
$O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O_2 \quad E^\ominus = +0.68\ V$

$E^\ominus_{cell} = (+1.33) – (+0.68) = +0.65\ V > 0 \Rightarrow$ energetically feasible

$Cr_2O_7^{2-}$ will be reduced by H_2O_2 to form back Cr^{3+} if H_2O_2 is not removed.

3 **(b)** **(iv)** When heated, H_2O_2 readily decomposes to O_2 and H_2O. Heating can be stopped when there is no more oxygen gas evolved to relight a glowing splint.

(c) **(i)**



(ii) Extreme heat will disrupt the van der Waals' forces in the tertiary and quaternary structures and the hydrogen bonds in the secondary, tertiary and quaternary structures of the protein. This alters the shape of the active site of the enzyme. The enzyme is denatured and loses its catalytic activity. Hence, the rate falls.

(d) **(i)** $\Delta S^{\ominus}$ is positive as protein unfolding proceeds with an increase in disorder when the protein unfolds from its regular structure into random coils.

(ii) $\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$
$0 = (+200) - T(+0.600)$
$T = 333\text{ K}$

3 **(d)** **(iii)** Using $\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$,
$\Delta G^{\ominus} = (+200) - 340(+0.600) = -4.00\text{ kJ mol}^{-1}$

Using $\Delta G^{\ominus} = -RT \ln K_c$,
$-4.00 \times 10^3 = -8.31 \times 340 \times \ln K_c$
$K_c = 4.12$

$$K_c = \frac{[\text{unfolded state}]_{\text{eqm}}}{[\text{folded state}]_{\text{eqm}}} = \frac{4.12x}{x}$$

$$\text{Proportion of folded protein} = \frac{[\text{folded state}]_{\text{eqm}}}{[\text{folded state}]_{\text{eqm}} + [\text{unfolded state}]_{\text{eqm}}}$$

$$= \frac{x}{x + 4.12x}$$

$$= 0.195$$

(e) Since $-CH(CH_3)CH_2CH_3$ side chain of isoleucine residue is larger and thus has a greater number of electrons/ larger electron cloud as compared to $-CH_3$ side chain of alanine residue, its side chain forms stronger van der Waals' forces with the side chain of another amino acid residue.

Hence, magnitude of $\Delta H^{\ominus}$ for the unfolding of the mutant protein is most likely higher.

4 (a) (i) Crushing of solid into fine powder would increase the total surface area and increase the frequency of effective collisions between reactant particles. Hence, this increases the rate of dissolving solid.

(ii)

$$M(OH)_2 + 2HCl \rightarrow MCl_2 + 2H_2O$$

Since $\mathbf{M}(OH)_2 \equiv 2HCl$,

$$\text{amt of } \mathbf{M}(OH)_2 \text{ in } 27.90 \text{ cm}^3 = \frac{1}{2} \times \frac{25.0}{1000} \times 0.000250$$

$$= 3.13 \times 10^{-6} \text{ mol}$$

$$\text{solubility of } \mathbf{M}(OH)_2,\ x = \left(3.13 \times 10^{-6}\right) \div \frac{27.90}{1000}$$

$$= 1.20 \times 10^{-4} \text{ mol dm}^{-3}$$

$$M(OH)_2(s) \rightleftharpoons M^{2+}(aq) + 2OH^-(aq)$$

eqm conc /mol dm^{-3}: x, $2x$

where x is the solubility of $M(OH)_2$, in mol dm^{-3}, in water at 25 °C

$$K_{sp} \text{ of } \mathbf{M}(OH)_2 = \left[\mathbf{M}^{2+}\right]\left[OH^-\right]^2$$

$$= (x)(2x)^2 = 4x^3$$

$$= 4\left(1.12 \times 10^{-4}\right)^3$$

$$= 5.62 \times 10^{-12} \text{ mol}^3 \text{ dm}^{-9}$$

(iii) Reagent : NaOH(aq) or NH_3(aq)

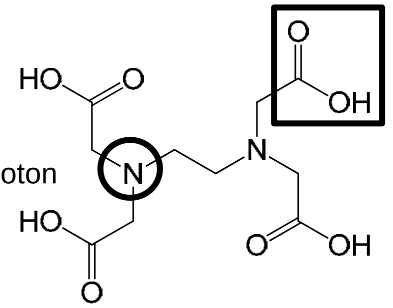
Observation : For both, white ppt is formed.

If **M** is Zn, white ppt is soluble in excess to give a colourless solution but if **M** is Mg, white ppt is insoluble in excess.

(iv) Since the salt formed is $MgCl_2$ and it has a pH of 6.5, the best indicator to be used is bromothymol blue.

The colour change is yellow to green.

(b) (i)



I *OR* accepting proton

II *OR* donating proton

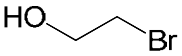
(ii) The p–p orbital overlap results in the delocalisation of lone pair of electron over the two O atoms in the anion of EDTA, hence dispersing the negative charge and stabilises its anion more than that of **P**. Hence, EDTA is a stronger acid than **P**.

(iii) Due to steric hindrance caused by the bulky benzene ring in **P**, the lone pair of electron on N atom is less available for protonation. Hence, **P** is a weaker base and has a lower 1st K_b value than EDTA.

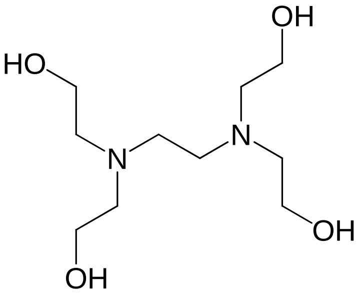
4 **(c)** **(i)** Y^{4-}

(ii) Basic buffer containing NH_3 and NH_4Cl buffered at <any value above pH 10.2>.

(d) **(i)** **Q**:



R:



(ii) Step 1: $Br_2(aq)$

Step 2: limited $NH_2CH_2CH_2NH_2$, ethanol, heat in sealed tube

Step 3: acidified $KMnO_4(aq)/K_2Cr_2O_7(aq)$, heat under reflux

5 **(a)** **(i)** Anode : $2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$

Cathode: $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

(ii) Amount of $Cl_2 = \dfrac{100 \times 10^6}{2 \times 35.5} = 1.41 \times 10^6$ mol

Since $Cl_2 \equiv 2e^-$,

$n_e = 2 \times 1.41 \times 10^6 = 2.82 \times 10^6$ mol

$Q = 2.82 \times 10^6 \times 96500 = 2.72 \times 10^{11}$ C

$I = \dfrac{2.72 \times 10^{11}}{24 \times 60 \times 60} = 3.15 \times 10^6$ A

(iii) When the diaphragm was removed, Cl_2 and NaOH will undergo disproportionation reaction to form ClO^-/NaClO.

$Cl_2(g) + 2OH^-(aq) \rightarrow Cl^-(aq) + ClO^-(aq) + H_2O(l)$

OR

$Cl_2(g) + 2NaOH(aq) \rightarrow NaCl(aq) + NaClO(aq) + H_2O(l)$

(iv) $F_2 + 2e^- \rightleftharpoons 2F^-$ +2.87 V ---(1)

$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$ +1.23 V

At the anode,

H_2O is oxidised in preference over F^- as $E^\ominus(O_2/H_2O)$ is less positive than $E^\ominus(F_2/F^-)$. Thus O_2 is formed.

(a) **(v)** In concentrated NaF(aq),

higher [F^-] causes equilibrium position of (1) to shift to the left, causing $E(F_2/F^-)$ becomes less positive.

However, since $E^{\ominus}(F_2/F^-)$ is much more positive than $E^{\ominus}(O_2/H_2O)$), $E(F_2/F^-)$ is still more positive than $E^{\ominus}(O_2/H_2O)$.

Hence, H_2O is still oxidised in preference instead of F^- and O_2 not F_2 will be obtained.

(b)

Hydrogen Halides	Observations
HBr	Red-brown fumes of bromine observed. $2HBr(g) + H_2SO_4(l) \rightarrow 2\ H_2O(l) + SO_2(g) + Br_2(g)$
HI	Violet fumes *OR* black solid of iodine observed. $2HI(g) + H_2SO_4(l) \rightarrow 2H_2O(l) + SO_2(g) + I_2(g)$ $8HI(g) + H_2SO_4(l) \rightarrow 4I_2(g) + H_2S(g) + 4H_2O(l)$

(c) Initiation step

$$\mathrm{C}l_2 \xrightarrow{\mathrm{UV}} 2\mathrm{C}l\bullet$$

Propagation steps

$$\mathrm{CH_3C}l + \mathrm{C}l\bullet \longrightarrow \bullet\mathrm{CH_2C}l + \mathrm{HC}l$$

$$\bullet\mathrm{CH_2C}l + \mathrm{C}l_2 \longrightarrow \mathrm{CH_2C}l_2 + \mathrm{C}l\bullet$$

$$\mathrm{CH_2C}l_2 + \mathrm{C}l\bullet \longrightarrow \bullet\mathrm{CHC}l_2 + \mathrm{HC}l$$

$$\bullet\mathrm{CHC}l_2 + \mathrm{C}l_2 \longrightarrow \mathrm{CHC}l_3 + \mathrm{C}l\bullet$$

Termination steps (any two)

$$2\mathrm{C}l\bullet \longrightarrow \mathrm{C}l_2$$

$$\bullet\mathrm{CH_2C}l + \mathrm{C}l\bullet \longrightarrow \mathrm{CH_2C}l_2$$

$$\bullet\mathrm{CHC}l_2 + \mathrm{C}l\bullet \longrightarrow \mathrm{CHC}l_3$$

$$2\bullet\mathrm{CH_2C}l \longrightarrow \mathrm{CH_2C}l\mathrm{CH_2C}l$$

$$2\bullet\mathrm{CHC}l_2 \longrightarrow \mathrm{CHC}l_2\mathrm{CHC}l_2$$

5 **(d)** **S** undergoes vigorous oxidation
⇒ **S** is an alkene and there is a loss of 2C as

From the MF of S, there is only one C=C bond and from MF of T, 2C is lost
⇒ $(COOH)_2$ is formed after oxidative cleavage, which further oxidised to $2CO_3^{2-}$ (as CO_2 reacts with alkaline medium) and $2H_2O$.

T gives a positive triiodomethane test with alkaline I_2
⇒ **T** is a ketone having the $-COCH_3$ group

T undergoes acid-carbonate reaction with Na_2CO_3
⇒ **T** is a carboxylic acid

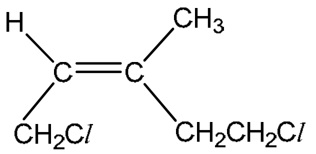
S undergoes nucleophilic substitution with KCN to form **U**
⇒ **S** is an alkyl halide, forming **U**, a nitrile.

U, both alkene and nitrile, is reduced to **V**, a saturated amine.

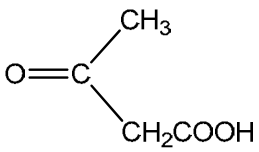
V undergoes acid-base reaction with HC*l*

U, a nitrile, undergoes acid hydrolysis with acid to form **W**, a carboxylic acid.

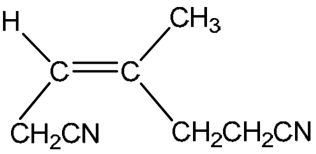
S:



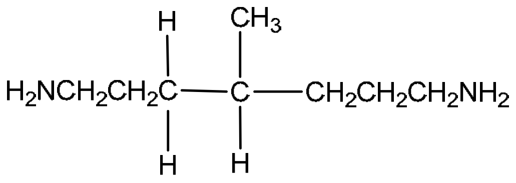
T:



U:



V:



$$H_2NCH_2CH_2\overset{H}{\underset{H}{C}}-\overset{CH_3}{\underset{H}{C}}-CH_2CH_2CH_2NH_2$$

W: