أولمبياد الكيمياء الدولي السابع والخمسون
الإمارات العربية المتحدة
57th ICHO - United Arab Emirates - 2025

IChO 2025

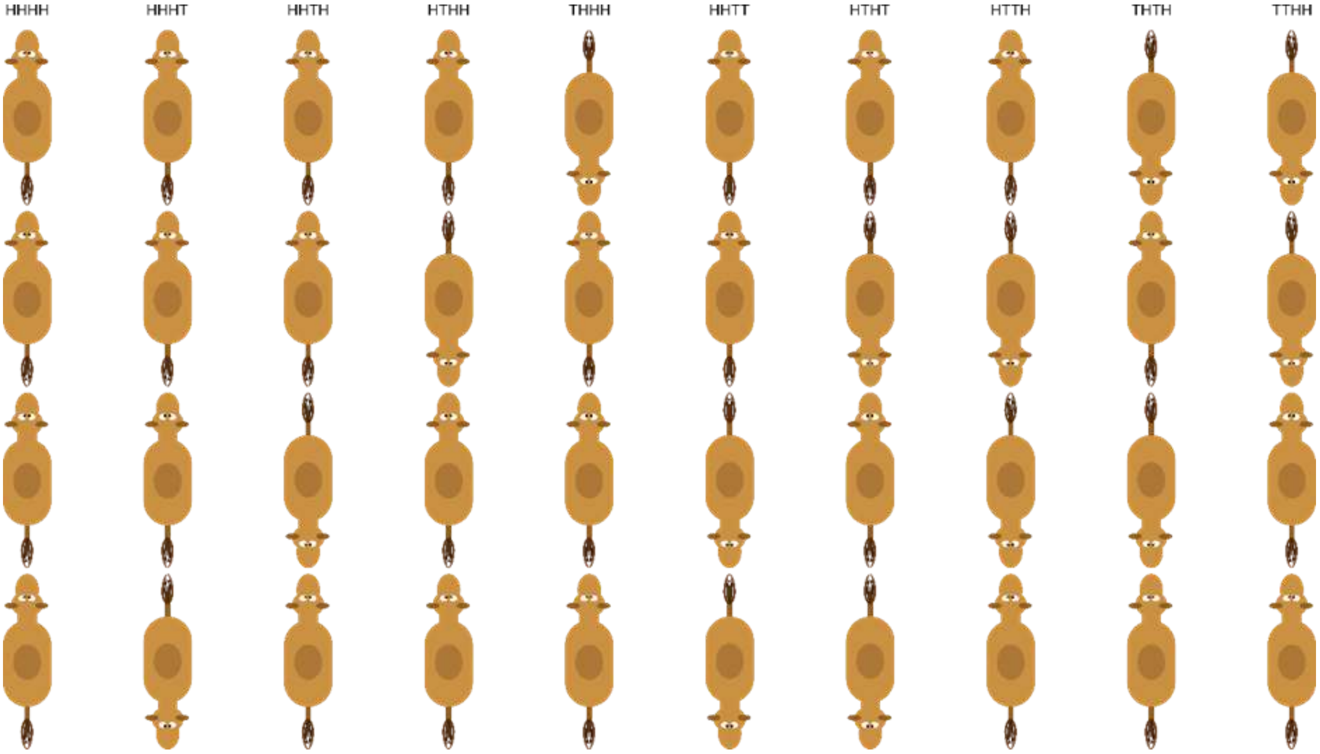
Solutions

Theory Prep Problems

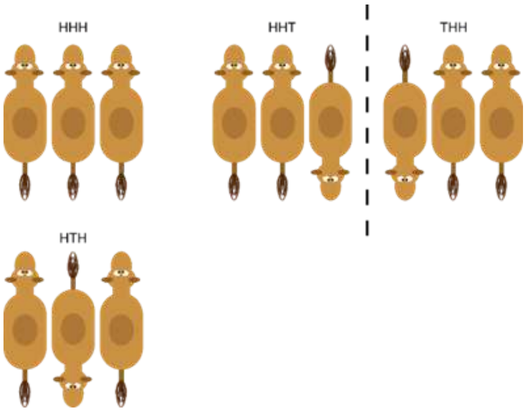
1. Stereocamelstry

(a) There are four possible arrangements: HHH, HHT, HTH, and THH.

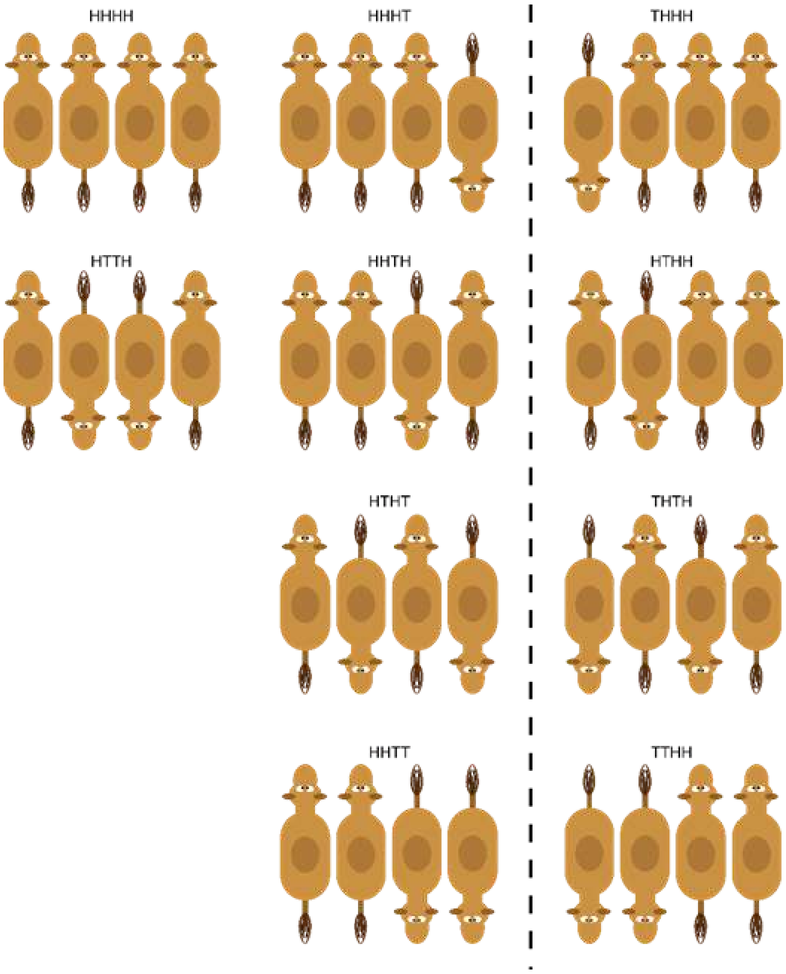
(b) There are ten possible arrangements: HHHH, HHHT, HHTH, HTHH, THHH, HHTT, HTHT, HTTH, THTH, TTHH.



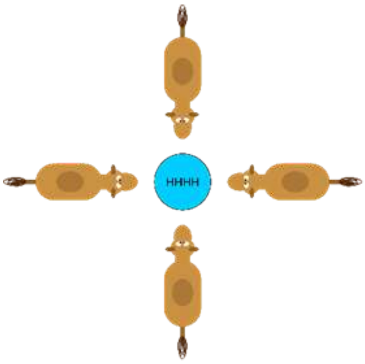
(c) There are four possible arrangements. The achiral arrangements are HHH and HTH. There is one pair of chiral arrangements (HHT and THH).

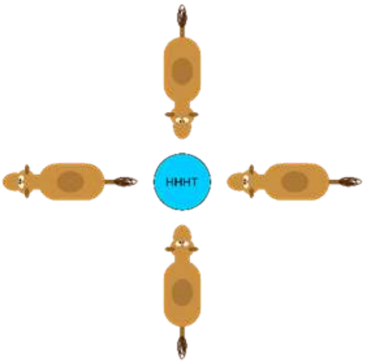


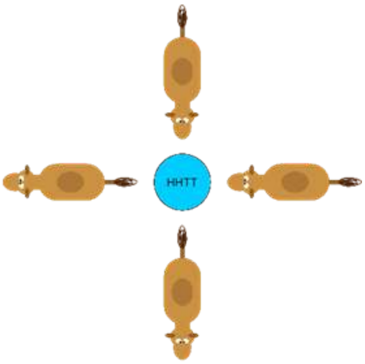
(d) There are ten possible arrangements. The achiral arrangements are HHHH and HTTH. There are four pairs of chiral arrangements (HHHT and THHH), (HHTH and HTHH), (HTHT and THTH), and (HHTT and TTHH).

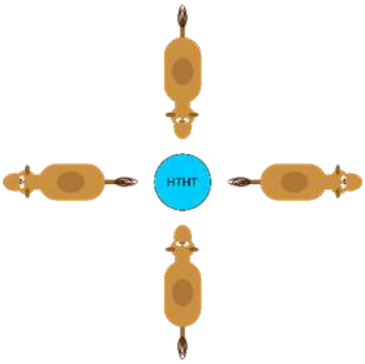


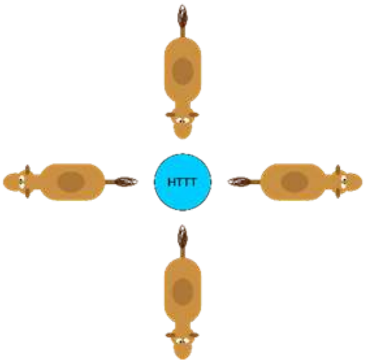
(e) There are six possible arrangements. All of them are achiral. Describing the arrangements clockwise from the 12 o’clock position, there is: HHHH, HHHT, HHTT, HTHT, HTTT, and TTTT.

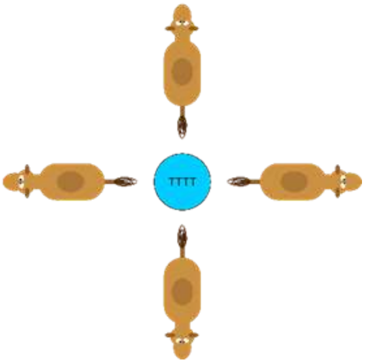




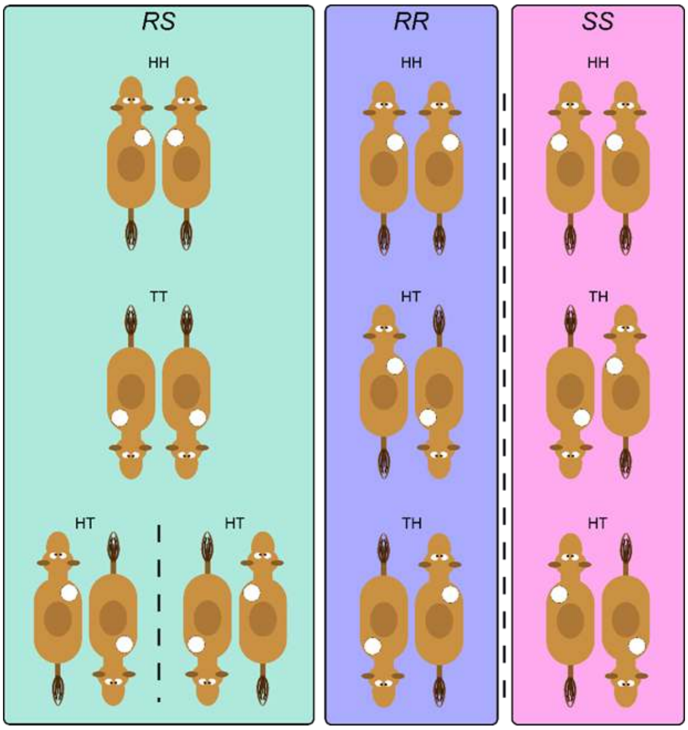




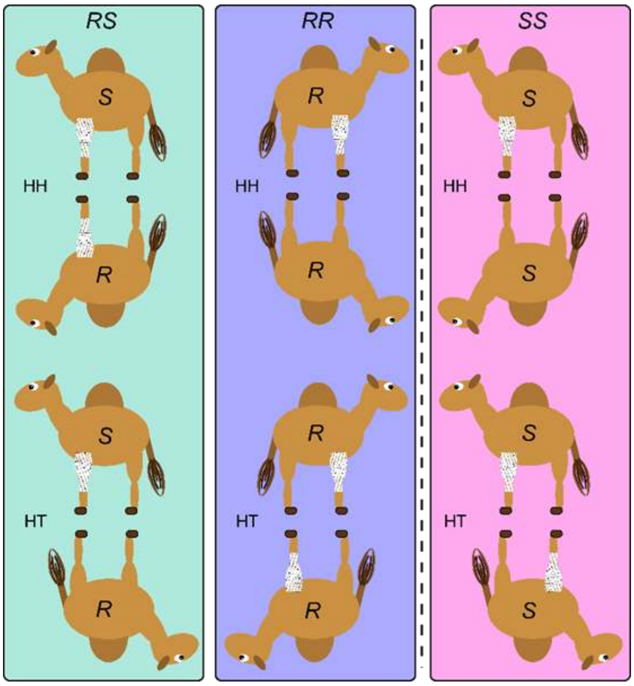




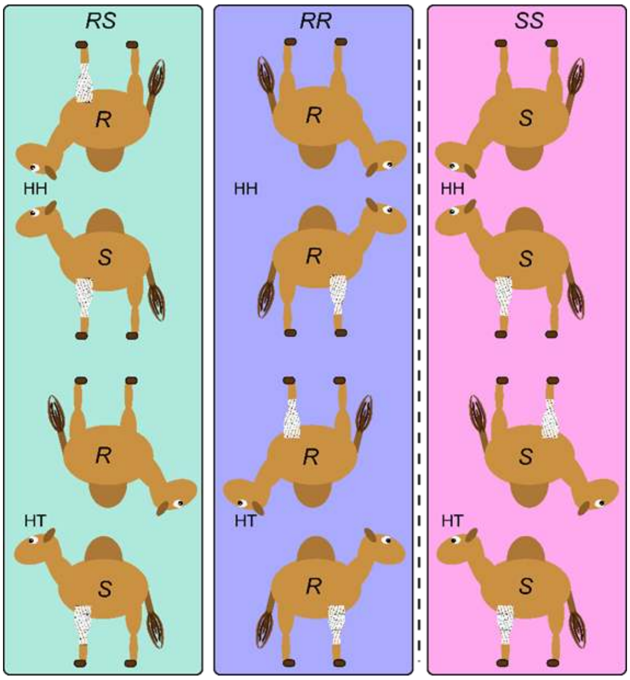
(f) There are ten possible arrangements. There are three possible arrangements where the two camels are both *R* (HH, HT, and TH). All three of these arrangements are chiral and their enantiomeric arrangements are the three possible arrangements where the two camels are *S*. There are four possible arrangements where one camel is *R* and one camel is *S* (HH, TT, HT, and TH). Note that this is one more arrangement than when the camels were individually achiral. Here, the HH and TT arrangements are not the same as one arrangement has the injured legs on the inside and one has the injured legs on the outside. The HH and TT arrangements are overall achiral as they both have mirror plane symmetry down the middle. The HT arrangement is the enantiomer of the TH arrangement.



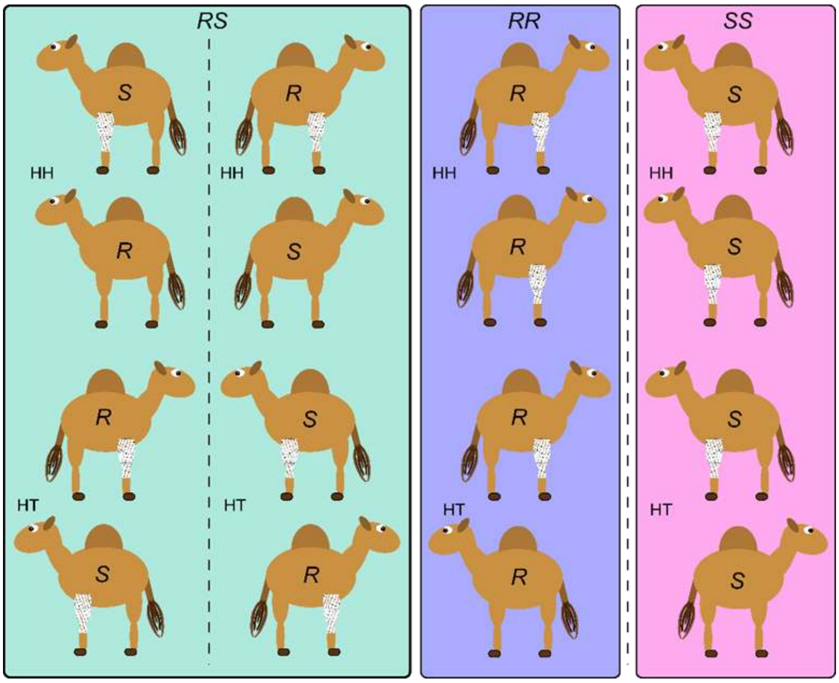
(g) There are six possible arrangements. There are two possible arrangements where the two camels are both *R* (HH and HT). Both arrangements are chiral, and their enantiomeric arrangements are the two possible arrangements where the two camels are *S*. There are two possible arrangements where one camel is *R*, and one camel is *S* (HH and HT). The HH and HT arrangements are both overall achiral. The HH arrangement has a mirror plane, and the HT arrangement has a centre of inversion.



(h) This is an identical situation to the previous one. There are six possible arrangements. There are two possible arrangements where the two camels are both *R* (HH and HT). Both arrangements are chiral, and their enantiomeric arrangements are the two possible arrangements where the two camels are *S*. There are two possible arrangements where one camel is *R*, and one camel is *S* (HH and HT). The HH and HT arrangements are both overall achiral. The HH arrangement has a mirror plane, and the HT arrangement has a centre of inversion.



(i) There are eight possible arrangements. There are two possible arrangements where the two camels are both *R* (HH and HT). Both arrangements are chiral, and their enantiomeric arrangements are the two possible arrangements where the two camels are *S*. There are now four possible arrangements where one camel is *R*, and one camel is *S*. There is one pair of enantiomeric HH arrangements and one pair of enantiomeric HT arrangements. There is no longer any mirror plane or centre of inversion symmetry in these *RS* arrangements. They differ in which camel has its hump closest and which camel has its feet closest to the other camel.

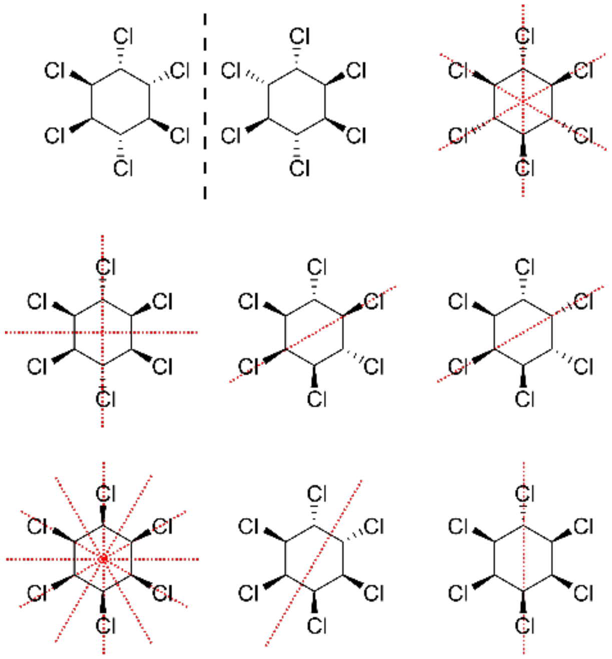

RS
RR
SS
S
R
R
S
HH
HH
HH
HH
R
S
R
S
R
S
R
S
HT
HT
HT
HT
S
R
R
S

2. Mirror, mirror plane on the wall, who's the deadliest of them all?

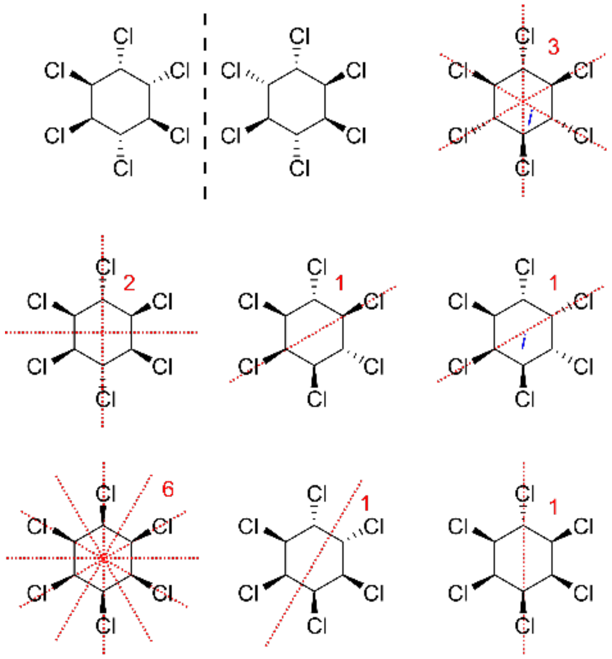
(a) $C_6H_6 + 3Cl_2 \rightarrow C_6H_6Cl_6$

The reaction proceeds via a free-radical addition reaction rather than a substitution reaction due to the relatively high strength of the C–H bonds. Whilst Faraday noted the formation of muriatic acid (now called hydrochloric acid), if the addition reaction proceeds cleanly then HCl is not formed. The HCl may have been from impurities in Faraday's samples. Modern techniques show that Faraday's starting material for the isolation of benzene likely was a mixture of at least 300 compounds.

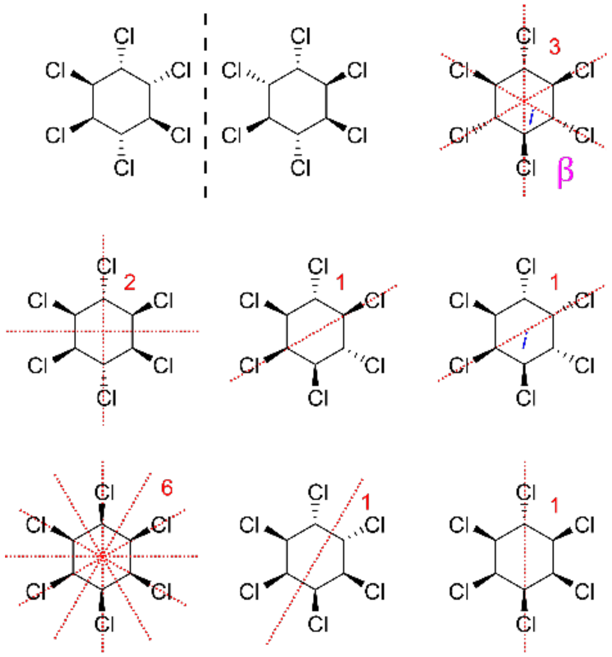
(b) The are nine stereoisomers of **HCH**. There is one pair of enantiomers and seven achiral structures. Mirror planes are identified with red lines.



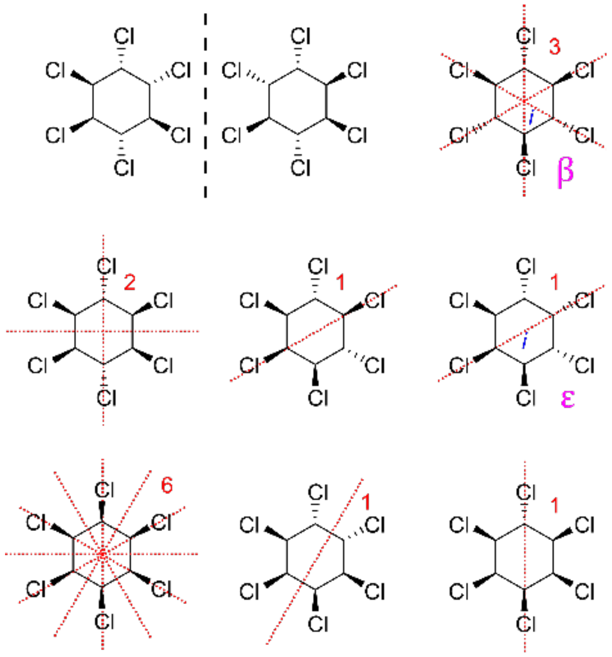
(c) First, we can count the number of planes of symmetry in each structure and label whether the structures have centre of inversion symmetry (*i*).



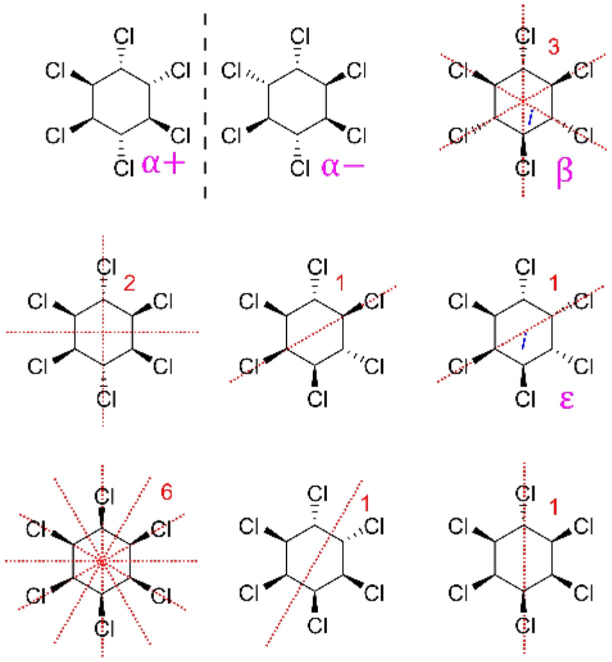
The most useful piece of information is the final clue: *The β isomer has by far the lowest chemical reactivity*. This is the isomer with the Cl atoms alternating on the top and bottom. See part **(d)** for explanation. This allows the β isomer to be assigned.



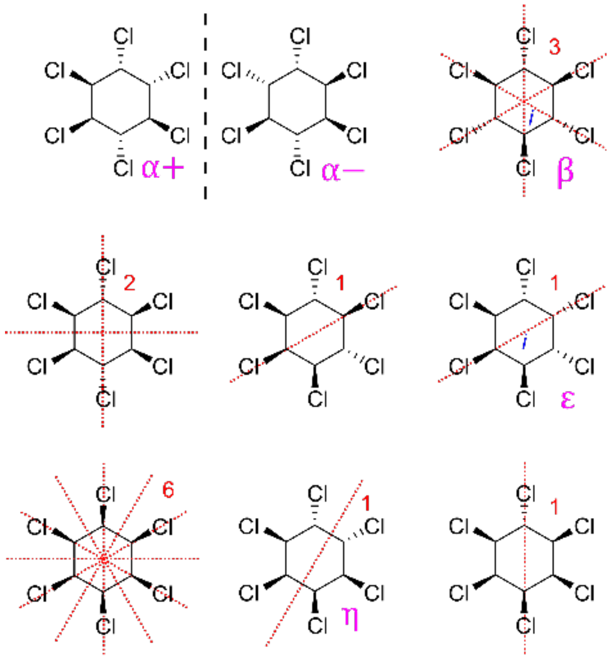
We can then use the first clue: *The β and ε isomers contain centres of inversion,* to identify the ε isomer.



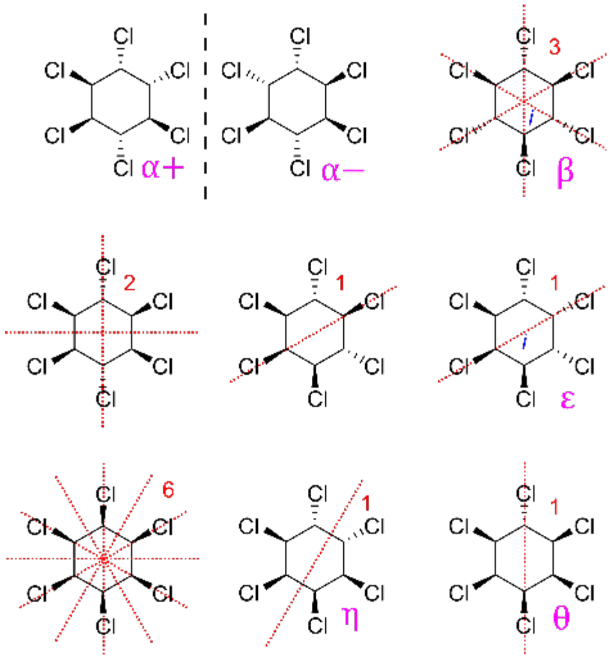
Only two of the nine isomers are chiral. Given we know from the sixth clue: *The + and – refer to dextrorotatory and levorotatory respectively*, it would make sense for the α+ and α− isomers to be the chiral ones. From the information given we cannot assign which is which, as +/− cannot be determined from chemical structure drawings. They have been assigned here for information.



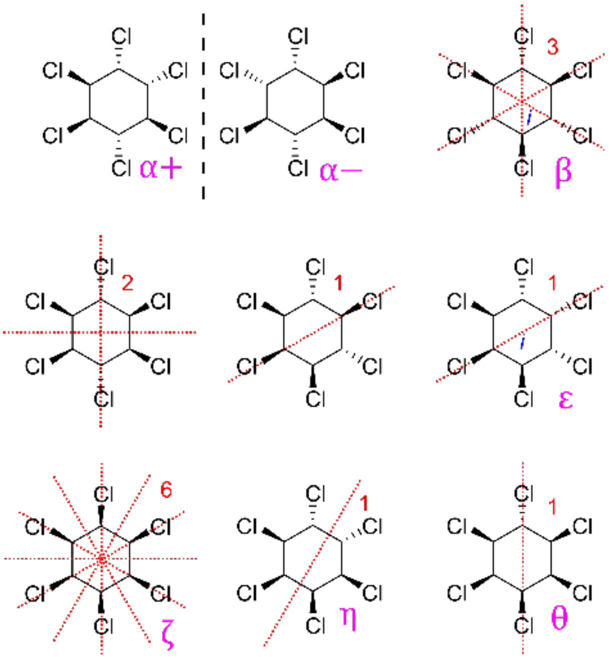
The fifth clue: *The η isomer does not possess a plane of symmetry through any of the atoms*, allows us to assign the η isomer, as this is the only one remaining with no plane of symmetry through any of the atoms.



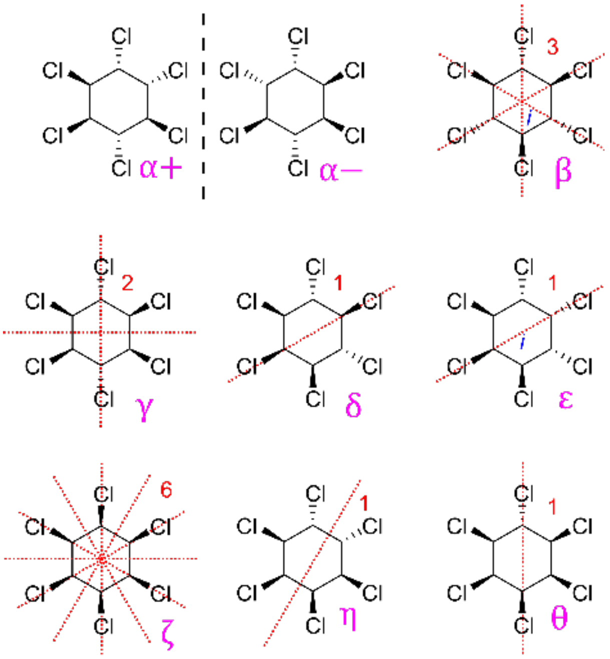
As epimers only differ in configuration at one centre, the third clue: *The θ isomer is an epimer of the η isomer*, now allows us to identity the θ isomer as there is only one compound that is an epimer of the η isomer remaining.



The second clue: *The ζ isomer is not an epimer of the α+ isomer*, now allows us to identify the ζ isomer.



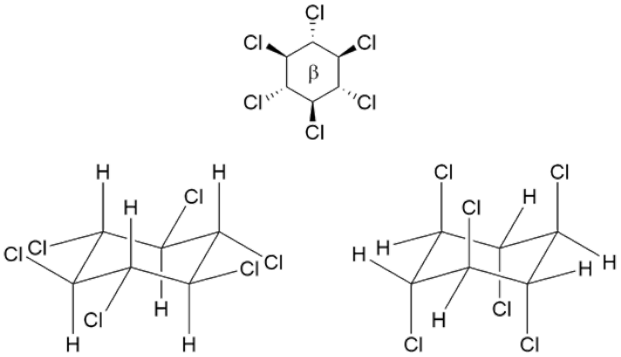
The fourth clue: *The γ isomer has more planes of symmetry than the δ isomer*, allows us to assign the γ isomer and the δ isomer to the remaining two structures.



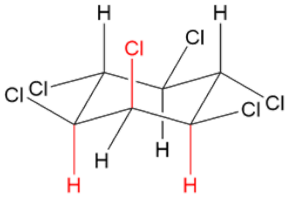
(d) The β isomer has the lowest chemical reactivity as this is the only isomer where all neighbouring Cl are *trans* to each other. Possible degradation pathways for **HCH** might include substitution or elimination. However, the presence of a Cl atom on each carbon sterically hinders the approach of nucleophiles, making substitution slow.

Elimination most readily proceeds via an antiperiplanar transition state. This requires a *trans* H and Cl (so both substituents must be in axial positions in a chair conformation). The β isomer is the only isomer which does not possess this in either possible chair conformation. The β isomer sits in the chair conformation with all Cl in equatorial positions (this is the only isomer where this is possible). The other chair conformation where all the Cl are axial is much higher in energy, however this is still not reactive as there is no *trans* H and Cl.

All the other isomers possess at least one *trans* H and Cl, which can sit antiperiplanar to each other in a chair conformation. Therefore, this makes the β isomer the least reactive.

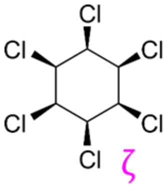


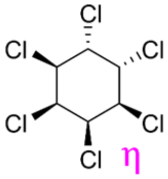
No antiperiplanar H and Cl in either chair conformation

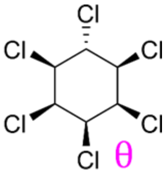


All other isomers can access one chair conformation which has at least one antiperiplanar H and Cl. This can eliminate HCl much more quickly.

(e) The ζ-**HCH**, η-**HCH**, and θ-**HCH** isomers all have at least four adjacent Cl atoms that are *cis* to each other (on the same face of the cyclohexane ring). Radical addition reactions are often not stereospecific, meaning all possible isomers can form. Cl is a much larger substituent than H, and so it becomes progressively less likely for additional Cl atoms to be added to the same face as existing Cl atoms over the course of the reaction due to steric hindrance, particularly on neighbouring atoms.


ζ

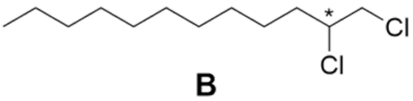

η


θ

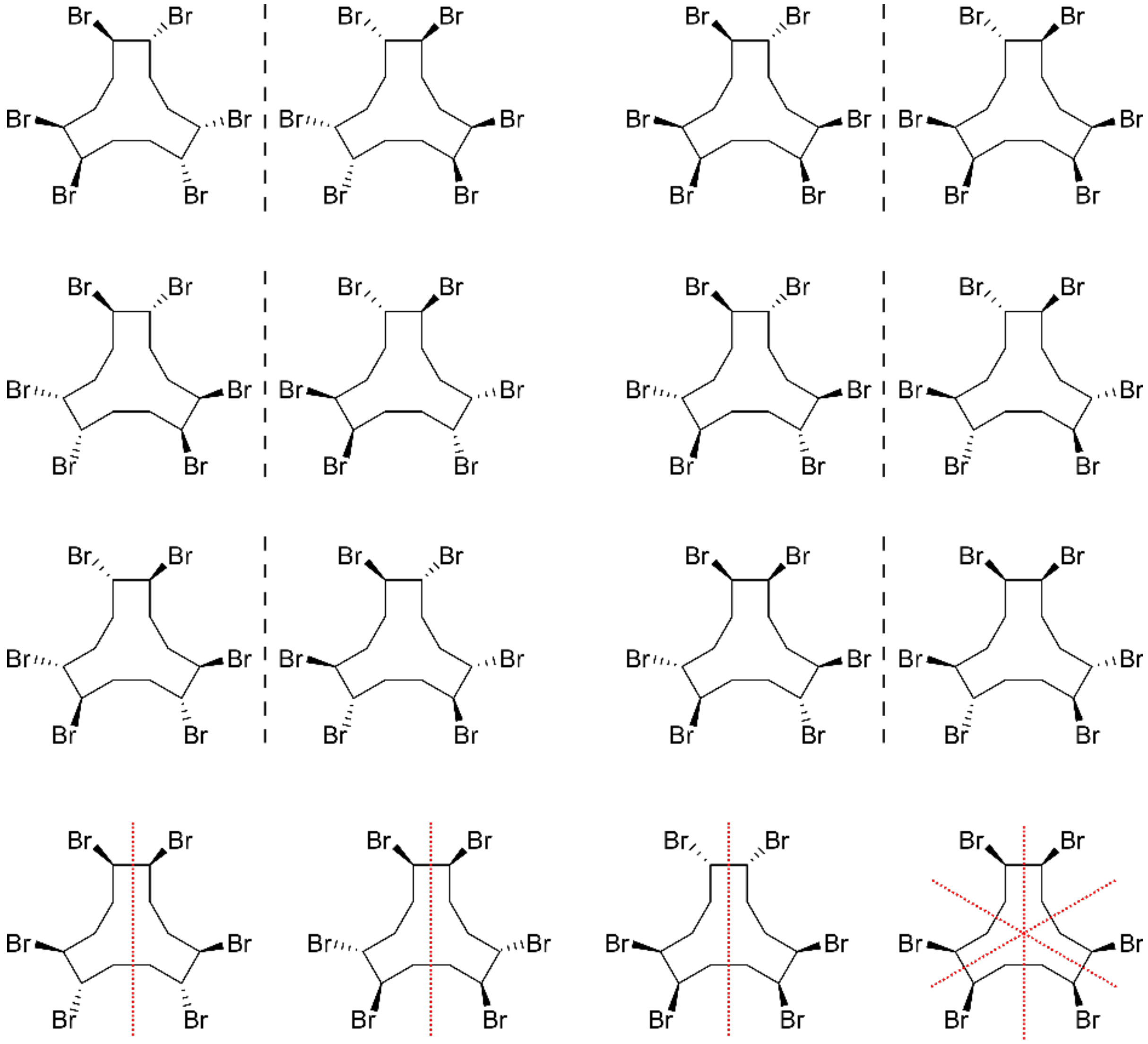
(f) The formula for **B** is $C_{12}H_{24}Cl_2$. The chlorine isotope pattern is the key indicator here. Cl is approximately 75% ^{35}Cl and 25% ^{37}Cl. We might first guess **B** contains two Cl atoms (formal addition of Cl_2 across one alkene). The relative intensity of the 240.122 peak compared to the 238.125 peak is consistent with this. Note the presence of ^{13}C complicates these isotope patterns. If product **B** contains two Cl, then its general formula must be $C_nH_{2n}Cl_2$. We can then work out that **B** is $C_{12}H_{24}Cl_2$.

(g) There are many possible chloroalkanes of formula $C_{12}H_{24}Cl_2$. The important clues here are that **B** was formed as a racemic mixture of two enantiomers and that **A** was chosen to be as simple/cheap as possible. Although we do not know the exact mechanism of the reaction, let's assume it is not stereospecific. The simplest/cheapest alkenes are terminal monosubstituted alkenes as there are no isomers to consider. Upon addition of Cl_2 across simple terminal monosubstituted alkenes, only the internal carbon becomes a stereocentre, so the best guess is the straight chain terminal alkene for **A**, and corresponding addition product of this **B**. The one stereocentre is marked with an *.

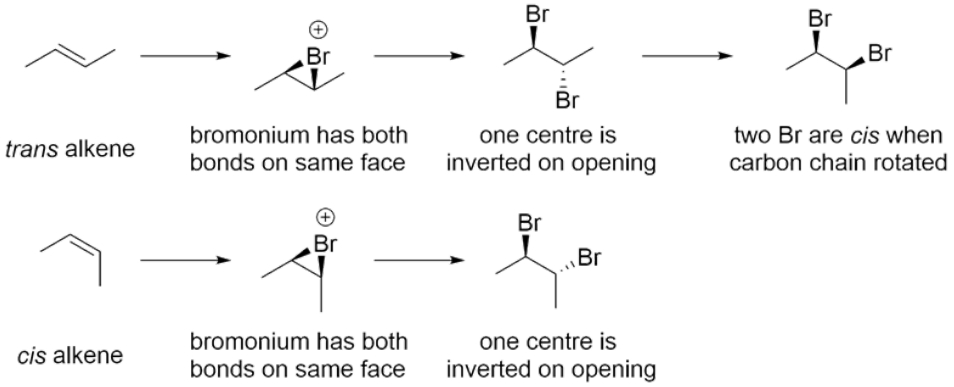

A

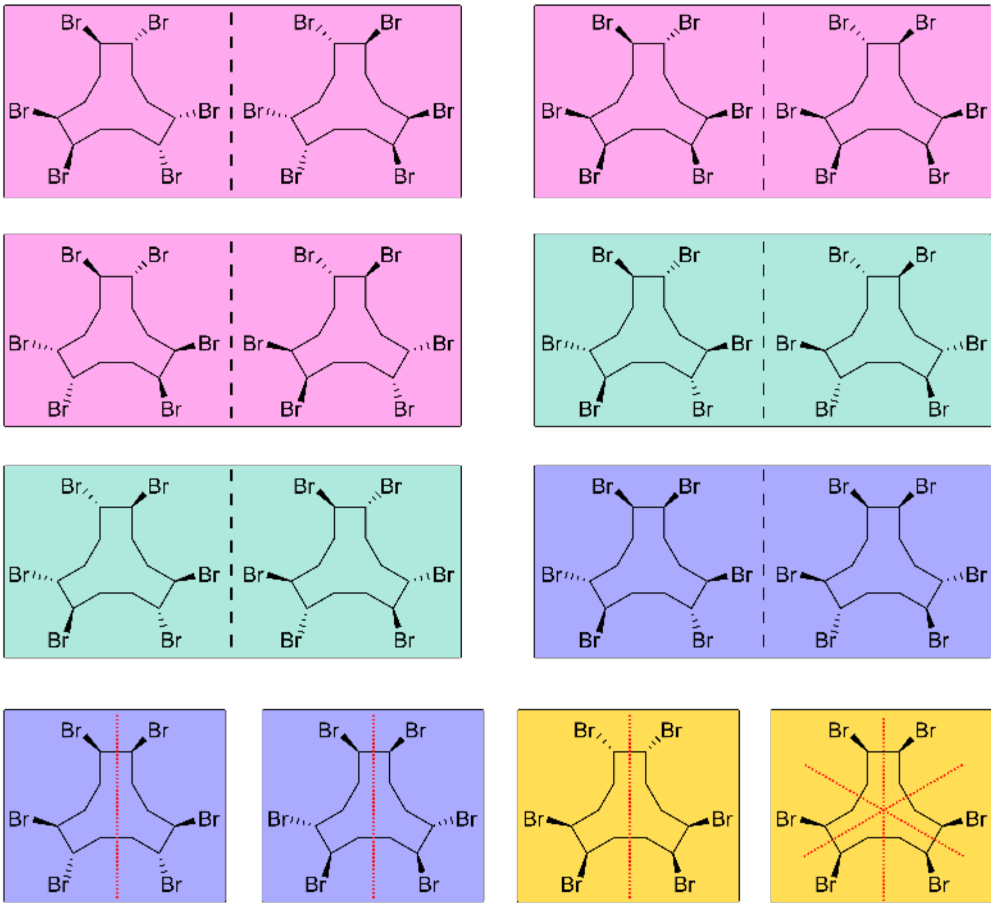

B

(h) There are 16 possible isomers. These consist of six pairs of enantiomers and four achiral diastereomers. The isomers have been drawn in such a way to show their maximum possible symmetry. Planes of symmetry have been shown by red lines.



(i) In a bromination reaction, the two bonds to the intermediate bromonium ion first form on the same face of the alkene. The bromide anion then attacks in at one of the two carbon atoms and inverts the stereochemistry of that centre only. Drawing the **HBCD** isomers in the way shown previously (to highlight any symmetry) has the carbon backbone in a *cis* conformation, rather than the more usual *trans*/staggered conformation. Thus, as drawn, when two Br are on the same face (*cis*) this must have come from a *trans* alkene, and when the two Br are on the opposite faces (*trans*) this must have come from a *cis* alkene.



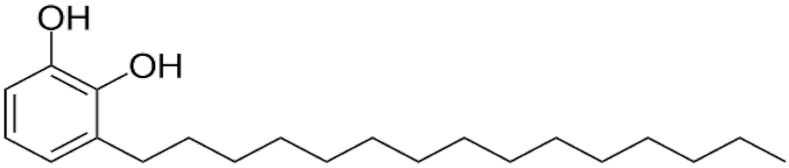


HBCD	All *cis*	*cis, cis, trans*	*cis, trans, trans*	All *trans*
Starting alkene	All *trans*	*cis, trans, trans*	*cis, cis, trans*	All *cis*

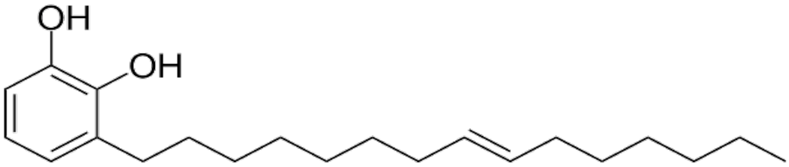
(j) No, it is not possible to tell which alkene was used as both the *cis, cis, trans*, and the *cis, trans, trans* alkenes give three different diastereomers as products. The commercial **HBCD** product is a mixture of the isomers coloured in pink, as the starting alkene is predominantly *cis, trans, trans*-cyclododeca-1,5,9-triene.

3. Urushiols

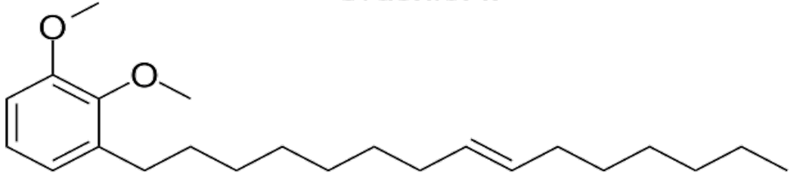
(a)



Urushiol I



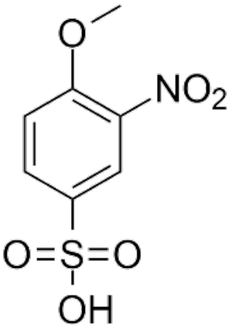
Urushiol II



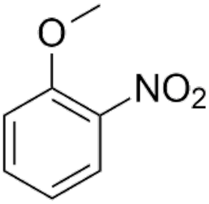
Dimethylurushiol II

For Urushiol II and Dimethylurushiol II both the *cis*- and the *trans*-isomer would be marked as correct with the given information.

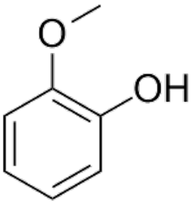
(b)



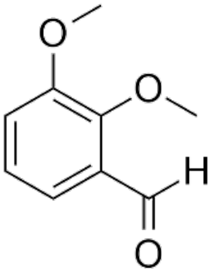
A



B



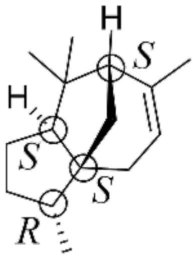
C



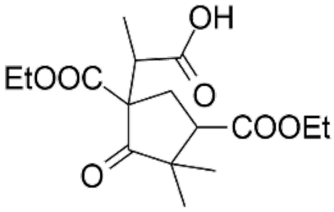
D

4. Cedrene

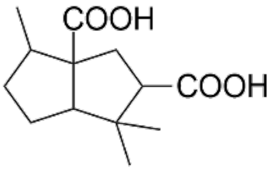
(a)



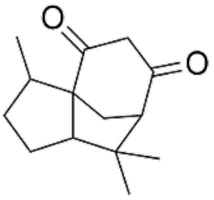
(b)



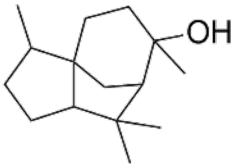
C



G



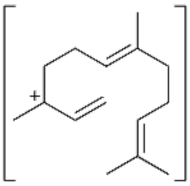
I



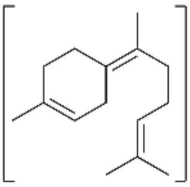
Cedrol

(c) ☑ **Li, NH_3** ☐ $LiAlH_4$ ☑ **H_2, Pd/C** ☐ HNO_3 ☐ H_2SO_4

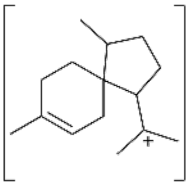
(d)



1

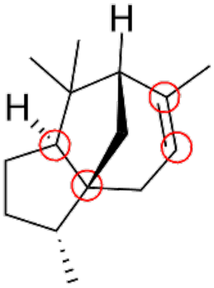


2



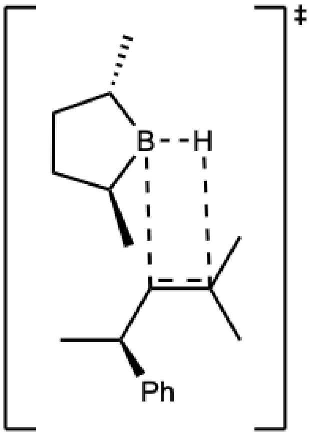
3

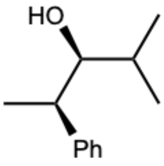
(e)



5. Stereochemical models

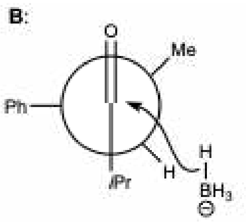
(a) This is the Masamune hydroboration reaction. Consider the chiral borane approaching from the top versus bottom face of the alkene. The four-membered ring transition state is favoured when the borane approaches from the top.

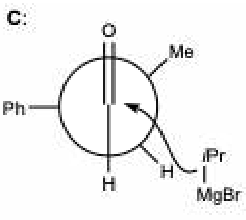




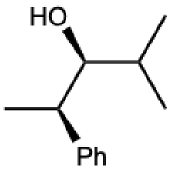
A

(b)

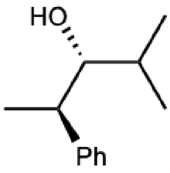




(c)



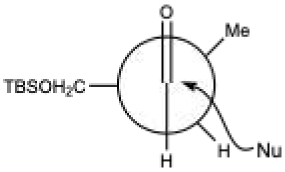
B



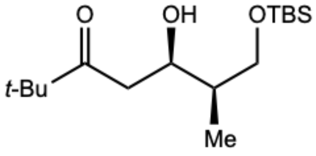
C

(d) ☑ **B**   ☐ C   ☐ Either B or C   ☐ Neither B nor C

(e)

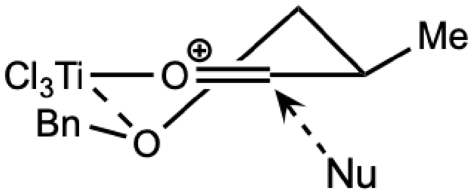


(f)



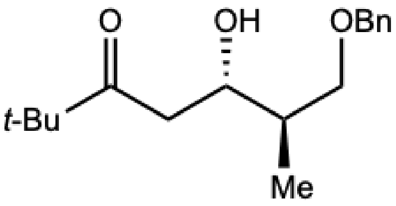
D

(g)



Nu approaches from the opposite side to Me. The twist boat does not form as the six-membered ring will just open to a lower energy geometry.

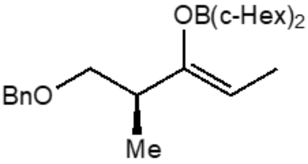
(h)



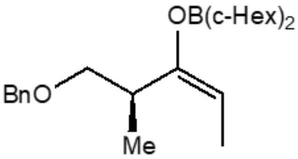
E

(i) Chelation of the Lewis acid $TiCl_4$ to both the carbonyl oxygen and benzyl oxygen. The steric bulk of OTBS in the previous case prevents the chelation of $TiCl_4$.

(j)

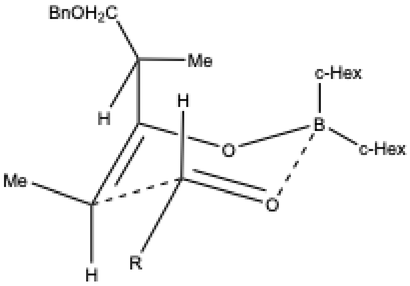


☐ *(Z)* - enolate



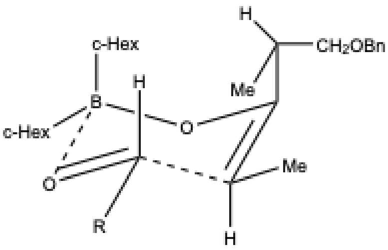
☑ *(E)* - enolate

(k) There are two possible transition state structures that can be proposed, **X** and **Y**.



X

Suggested by Houk Model

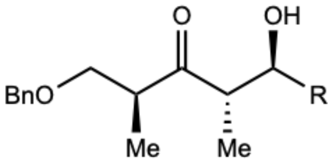


Y

Actual transition state based on experimental product

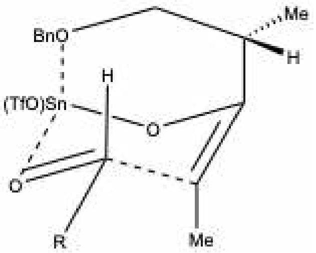
While **X** obeys the Houk model to minimise allylic strain, the transition state **Y** minimises steric strain between H and the large c-Hex groups on Boron and predicts the experimental product **F**.

(l)

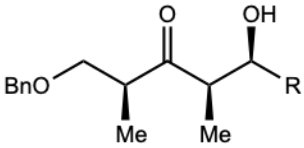


F

(m)



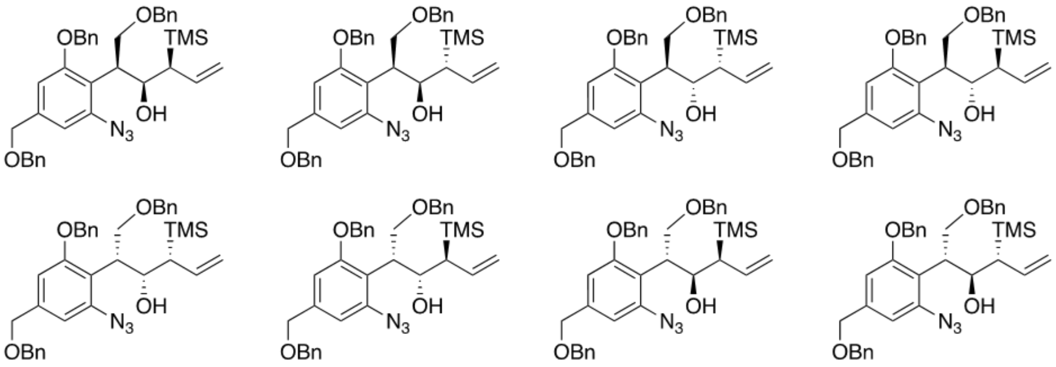
(n)



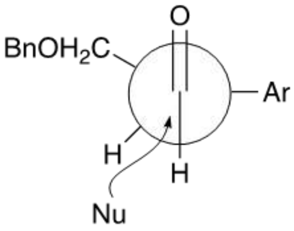
G

6. Stereocontrol in the synthesis of FR66979

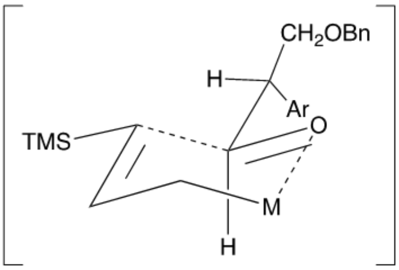
(a)



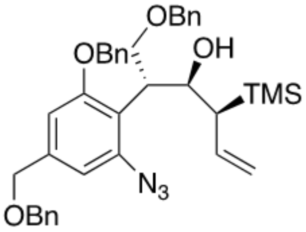
(b)



(c)

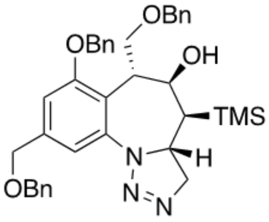


(d)

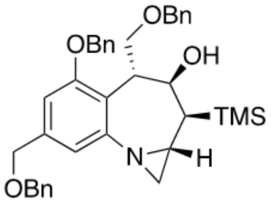


C

(e) Stereochemistry is not required.

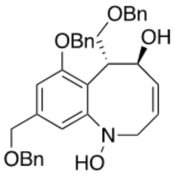


D

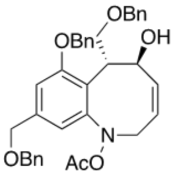


E

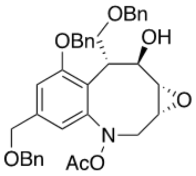
(f) Stereochemistry is not required.



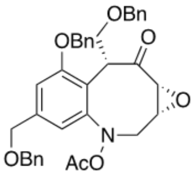
G



H



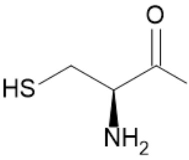
I



J

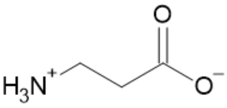
7. Coenzyme A and anaplerotic reactions

(a) There are two sulfur containing canonical amino acids, cysteine and methionine. Only the former one contains a free thiol group, which is donated to CoA. Thus, **X1** is cysteine. The absolute configuration of the stereocentre in **X1** is *R*.

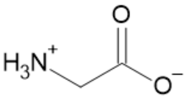


X1

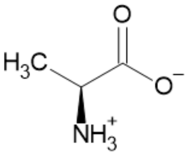
(b) **X2** is β-alanine, which is a homologue of glycine (**X3**) and structural isomer of alanine (**X4**)



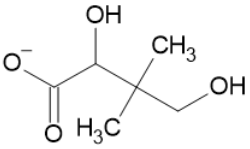
X2



X3

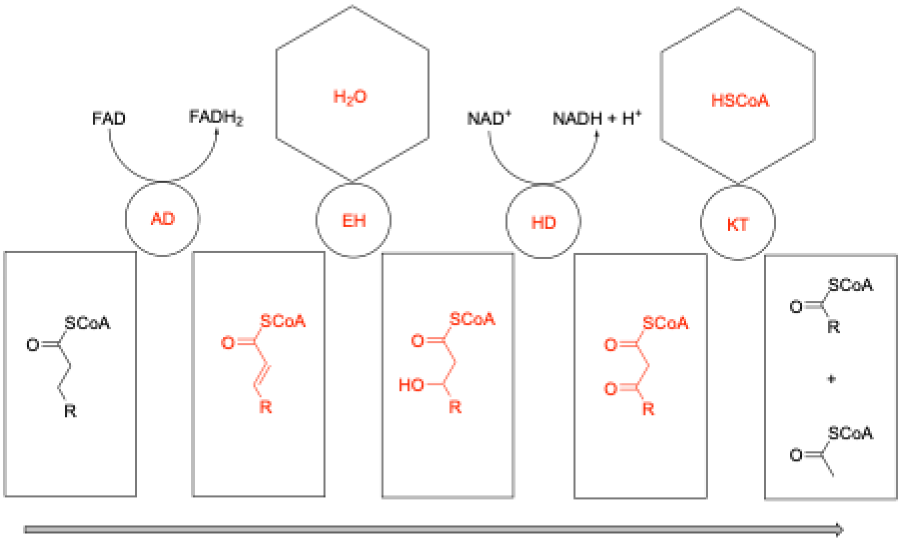


X4



Pantoate

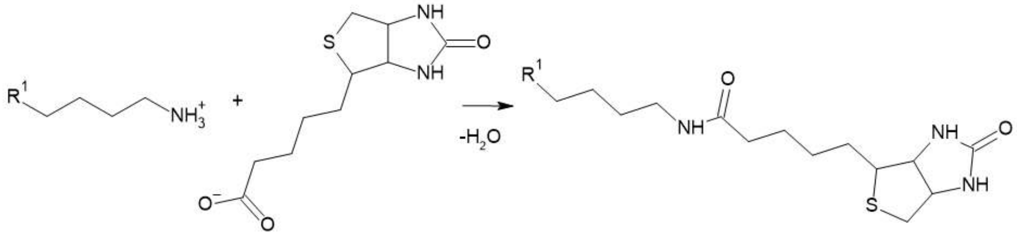
(c),(d),(e)



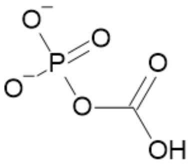
(f) The thiol group is the most readily oxidised one from the given list. The process of –SH oxidation can spontaneously develop in aerobic conditions and does not require co-enzymes or co-factors. Coenzyme A can protect the thiol groups from irreversible oxidation by forming intermolecular S-S bridges.

(g) Ligase. E_1 is pyruvate carboxylase.

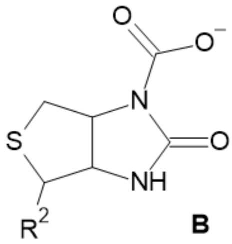
(h)



(i)

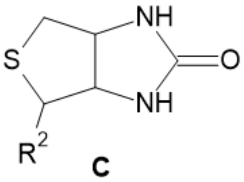


A

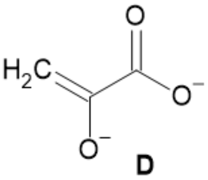


B

(j)

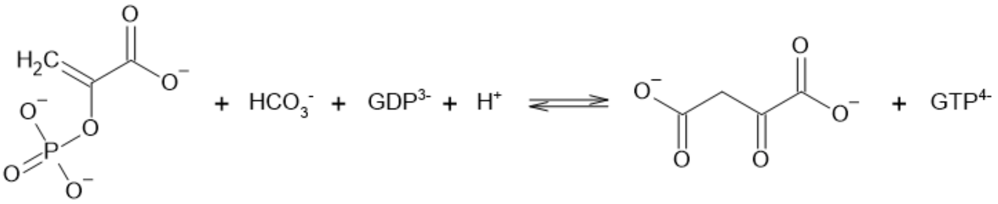


C



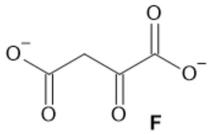
D

(k)

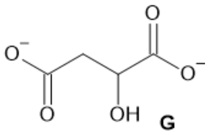


(l) The reverse reaction suggests that E_2 is a lyase, phosphoenolpyruvate carboxykinase. Since phosphoenolpyruvate (PEP) is a superhigh energy molecule, the excess energy left over after carboxylation is used to produce GTP. Complete usage of the PEP energy makes the reaction readily reversible.

(m)



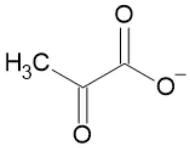
F



G

(n) Oxaloacetate and malate are also intermediates of the tricarboxylic acid cycle. Formation of malate from fumarate is reversible, which is responsible for partial distribution of ^{14}C between two carboxylic groups, when malate forms back from fumarate again. The carboxylate carbon next to the hydroxyl group in malate is retained in PEP and glucose.

(o)



H

(p) E_3 is a lyase, phosphoenolpyruvate carboxylase. By contrast to the E_2 catalysed reaction, GTP is not formed as one of the products. Accordingly, the E_3 catalysed reaction is actually irreversible. E_4 is an oxidoreductase, malate dehydrogenase (oxaloacetate-decarboxylating).

(q) E_5 is a kinase. Moreover, two substrates (pyruvate and inorganic phosphate) are phosphorylated because of this reaction, thus E_5 is typically referred to as dikinase or pyruvate, phosphate dikinase.

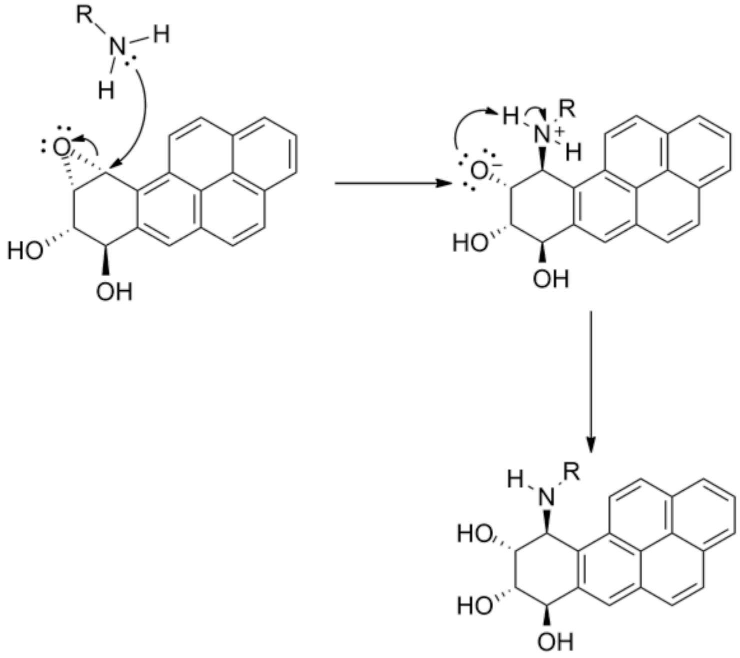
8. Why smoking is deadly

(a) Enzyme 1: Oxidase

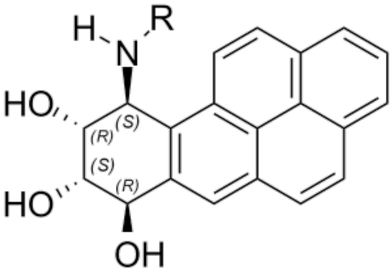
Enzyme 2: Hydrolase

Enzyme 3: Oxidase

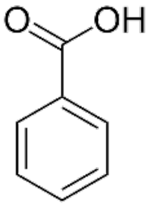
(b)



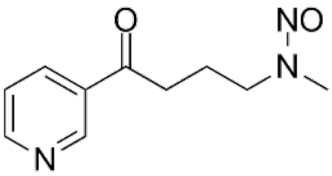
(c)



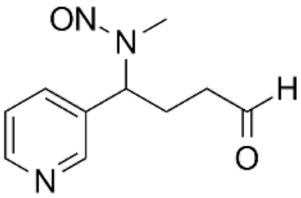
(d) The product is benzoic acid.



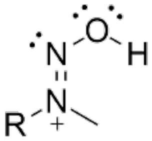
(e)



and

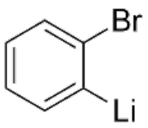


(f)

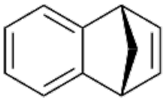


R

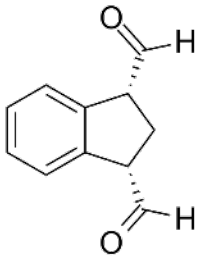
(g)



B

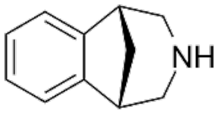


C

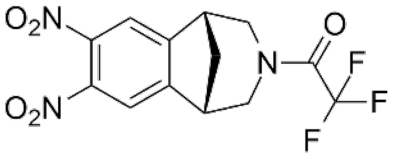


D

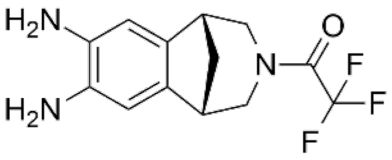
E



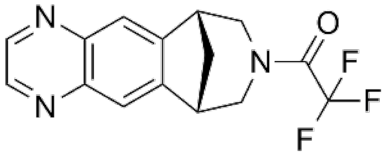
F



G



H



I

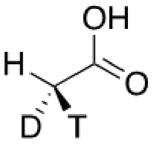
9. Determining the stereochemistry of enzymatic reactions

(a) In the original literature, this was performed with the following two steps:

1. O_3
2. I_2, KI, Na_2CO_3

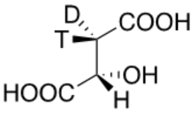
For the purpose of this question, any solution that suggests ozonolysis (or a more recent equivalent method from the literature) followed by iodine in basic conditions (iodoform reaction) can be accepted.

(b)

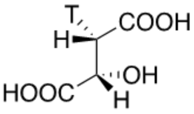


(*S*)-**B**

(c)



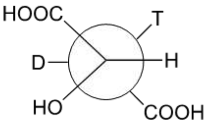
D



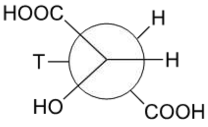
E

Note that the new stereocentre formed has (*S*)-configuration, and the original stereocentre is inverted. While this is drawn in the most stable conformation of **D** and **E**, a correct answer for this part can be in any conformation.

(d)



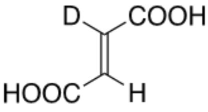
D



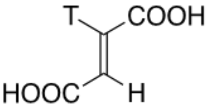
E

For this part, the Newman projection must be drawn in the most stable conformation, with the two COOH groups *anti* to each other. This helps to determine which hydrogen isotope is anti-periplanar to OH and gets eliminated as water in the next step.

(e)



F



G

(f)

F forms from **D**, and **G** forms from **E**, so **F** : **G** = 4 : 1

Thus, 80% of T activity will be lost after fumarase (as T is eliminated from **D** to **F**).

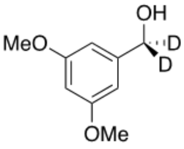
For (*S*)-**B**, ***Z*** = 0.2

(g)

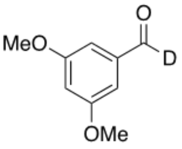
Similar analysis can be performed. Alternatively observe the symmetry of the system.

For *(R)*-**B**, ***Z*** = 0.8

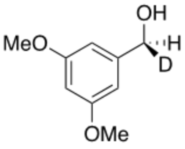
(h)



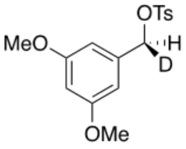
H



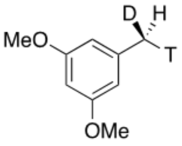
I



J



K



L

(i)

There are multiple possible methods:

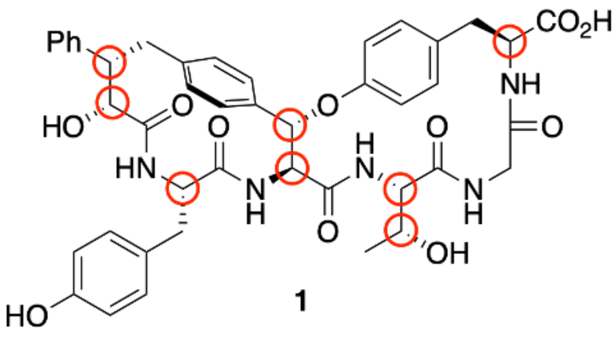
1) Use (–)-α-pinanyl-9-BBN.

2) Use deuterated (+)-α-pinanyl-9-BBN.

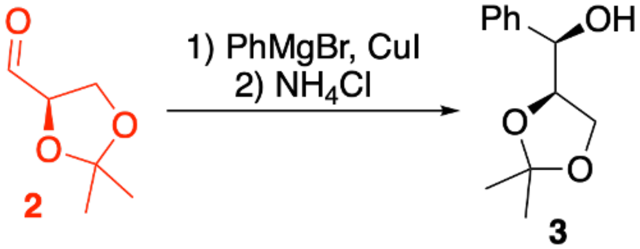
Other reasonable methods can be accepted.

10. The synthesis and derivatisation of natural products

(a)



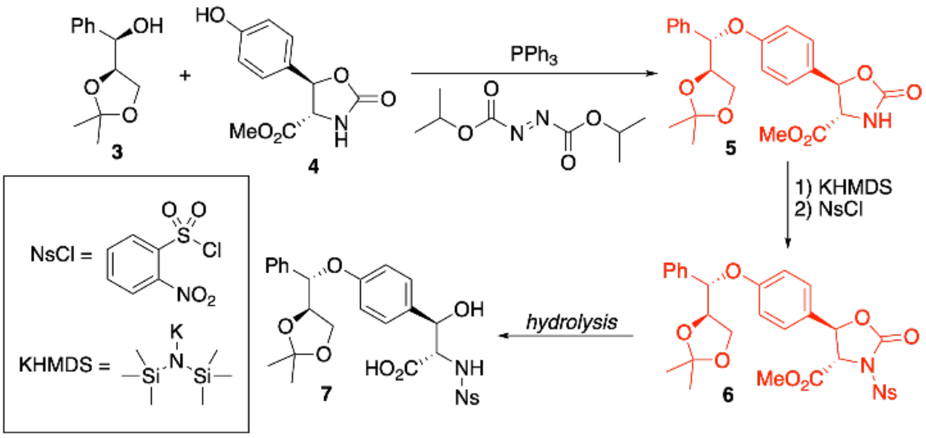
(b)



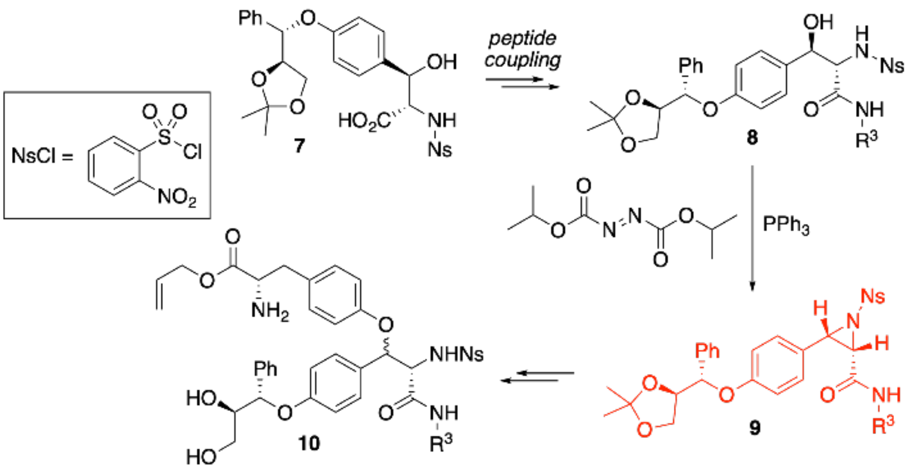
(c)

b. Felkin-Anh model with chelation

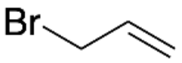
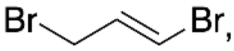
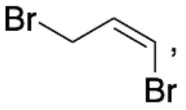
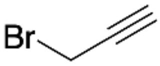
(d)



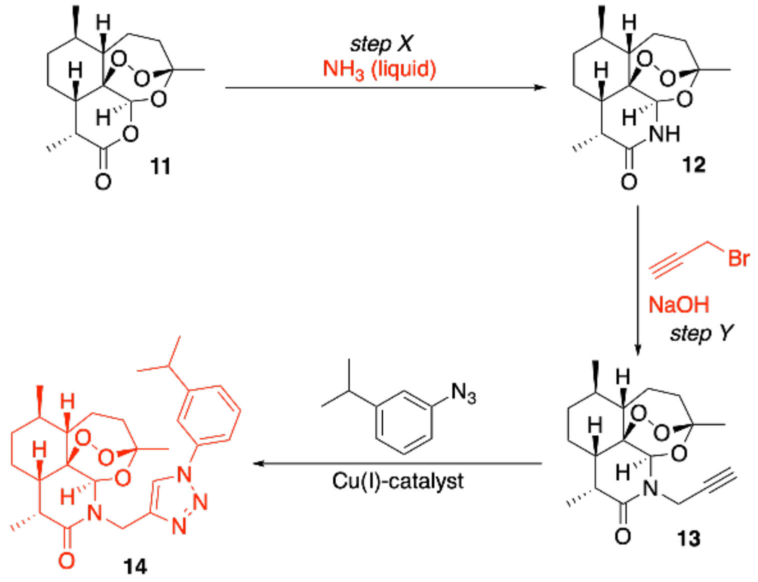
(e)



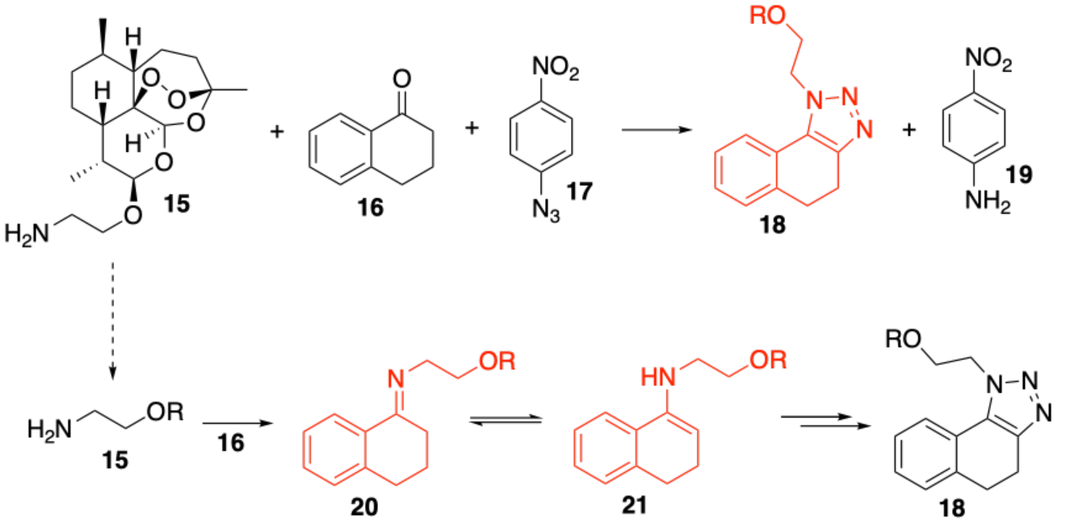
(f)

Reagent	Step	Reagent	Step
NMe_4Cl, H_2O		 , NaOH	
NH_2OH		 NaOH	
NH_3 (liquid)	X	 , NaOH	
NH_2NH_2		 , NaOH	Y

(g)


step X
NH3 (liquid)
11
12
Br
NaOH
step Y
13
N3
Cu(I)-catalyst
14

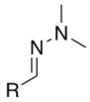
(h)


15
16
NO2
N3
17
RO
18
NO2
NH2
19
H2N
OR
15
16
N
OR
20
HN
OR
21
RO
18

11. A saga about imines

Episode IV: A new imine

(a) Compound **1** is a hydrazone; **2** is an oxime; **3** is an amidine; **4** is an imidoyl chloride; **5** is a heterocycle hexahydrotriazine (an aminal); **7** is an iminium cation; **8** is the aromatic heterocycle quinoline; **9** is a nitrone or an imine N-oxide; **10** is a substituted pyridine and dihydroimidazole (amidine). The rest of the compounds are imines (highlighted in red).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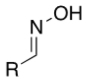
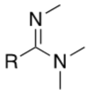

2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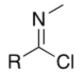
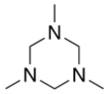
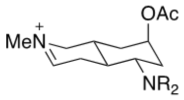

4


5


6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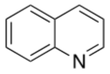
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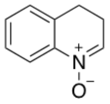
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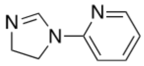
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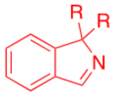
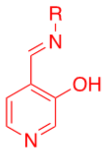
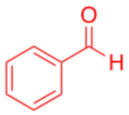
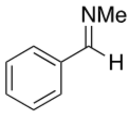
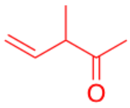
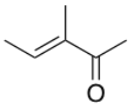
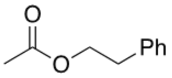
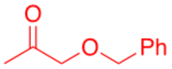
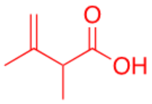
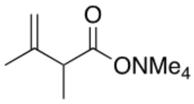
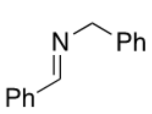

11


12

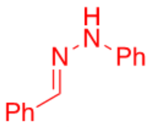
(b)

 **13**  **14**	 **19**  **20**
 **19**  **20**	 **21**  **22**

(c)

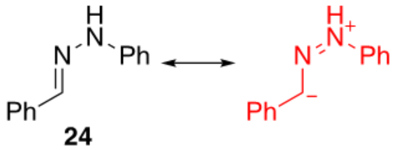


23



24

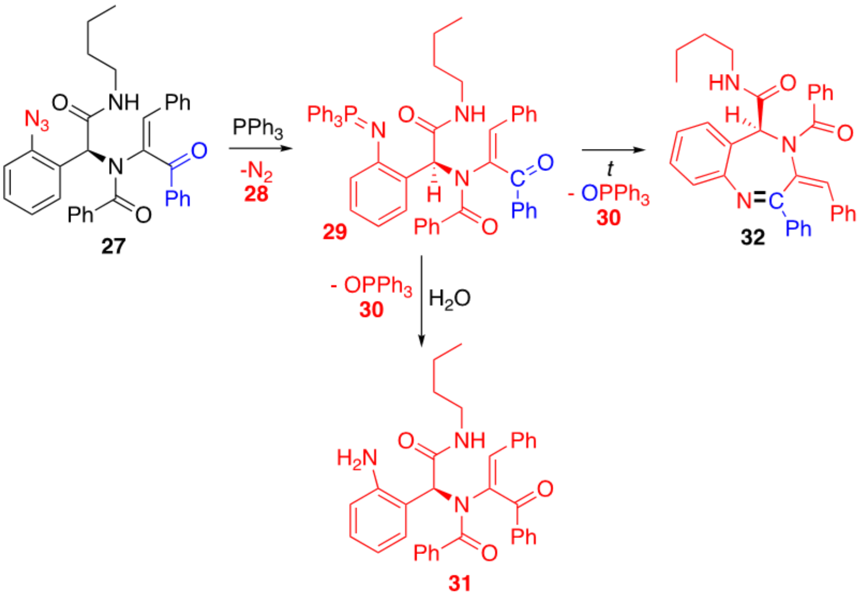
(d)



(e)

Condition(s) for **25**: AB	Condition(s) for **26**: B

(f) Compound **27** should have azido-group because it reacts with acetylene by copper catalyzed click reaction.



(g)

33: D

34: BEF

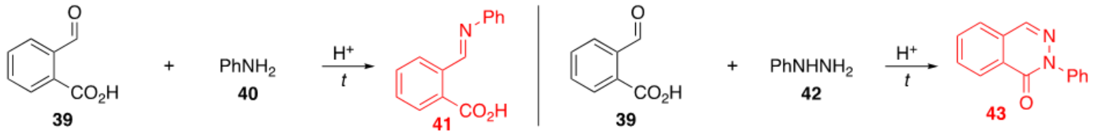
35: CF

36: CF

37: CF

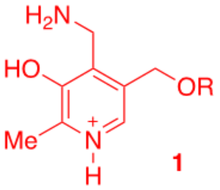
38: CF

(h)



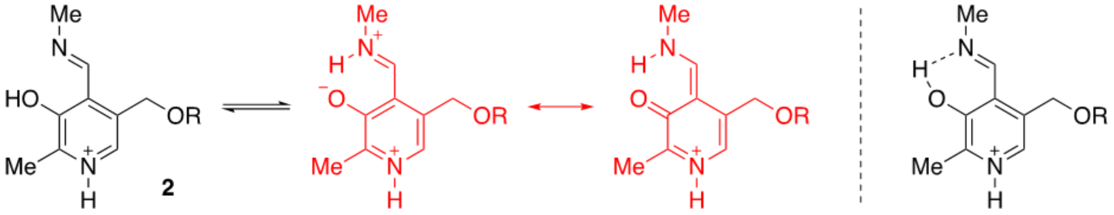
Episode V: The iminium salts strike back!

(i) Amines are usually more basic compared with imines. Nitrogen atoms with sp^3-hybridisation usually possess higher basicity than sp^2-hybridised nitrogens in the same environment.

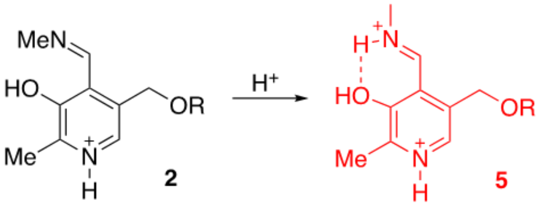


1

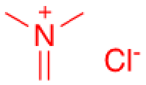
(j) The phenolic proton is very acidic due to the protonated state of pyridine.



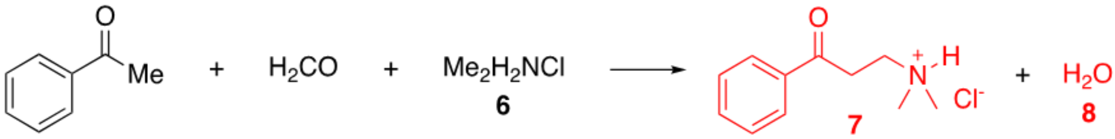
(k) Compound **5** is the more favourable reaction outcome: hydrogen bonding stabilises the C=N bond configuration.



(l)

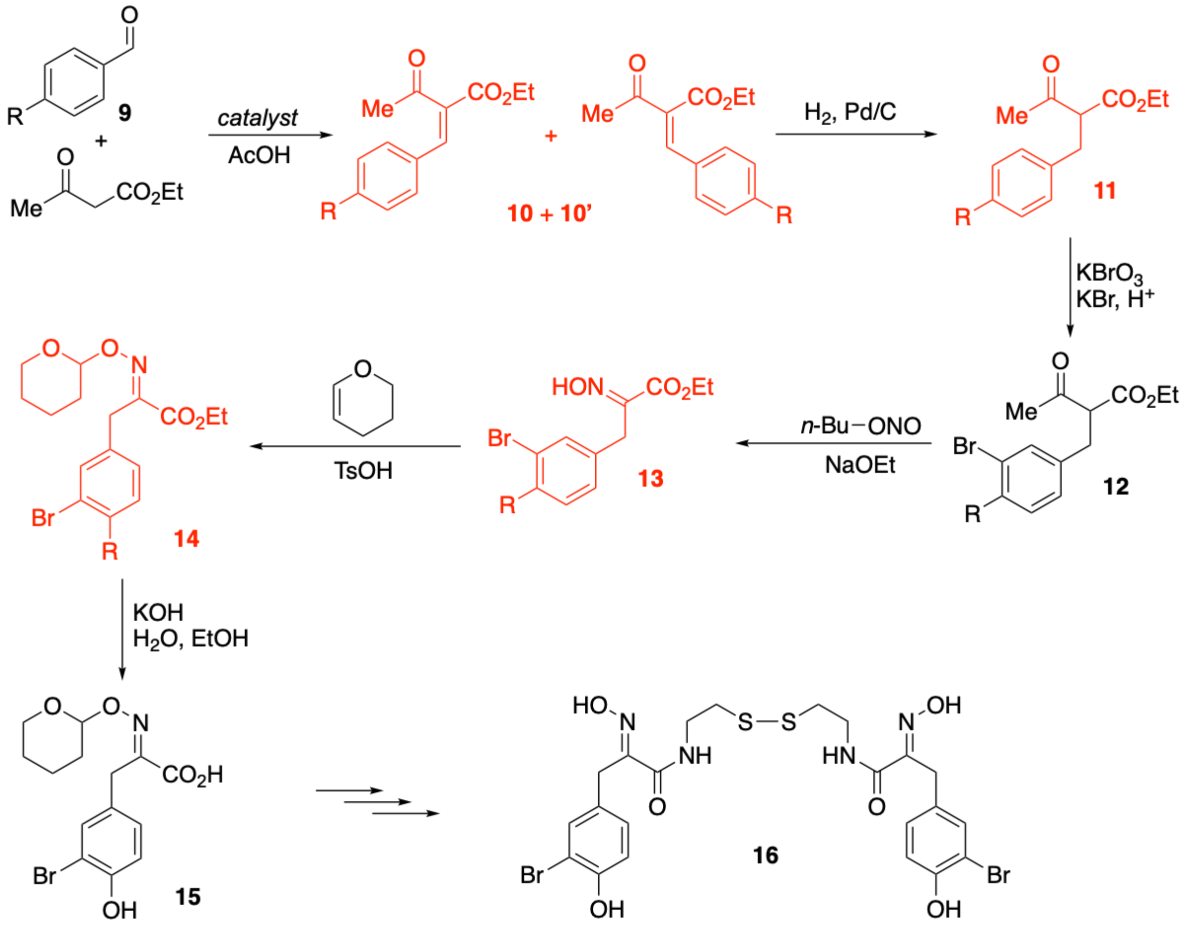


(m)

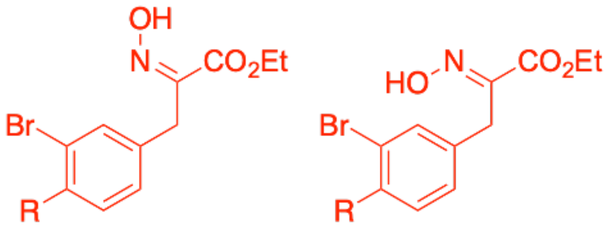

O
Me
+
H_2CO
+
Me_2H_2NCl
6
O
+
H
Cl^-
7
+
H_2O
8

(n) R = OH

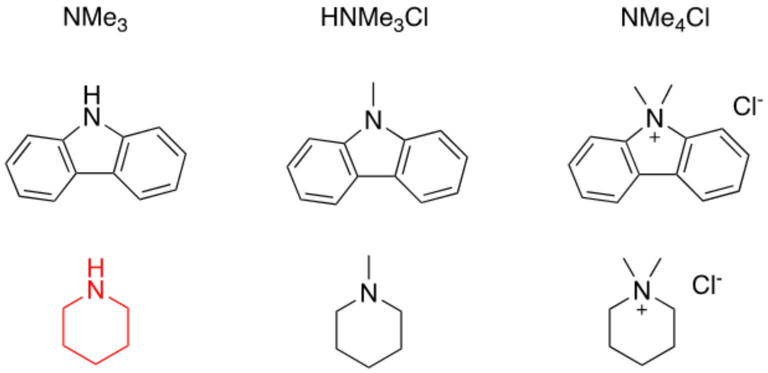
(o)


O
R
9
+
O
Me
CO_2Et
catalyst
AcOH
O
Me
CO_2Et
R
+
O
Me
CO_2Et
R
10 + 10'
H_2, Pd/C
O
Me
CO_2Et
R
11
$KBrO_3$
KBr, H^+
O
Me
CO_2Et
Br
R
12
n-Bu−ONO
NaOEt
HON
CO_2Et
Br
R
13
O
TsOH
O
O
N
CO_2Et
Br
R
14
KOH
H_2O, EtOH
O
O
N
CO_2H
Br
OH
15
HO
N
NH
S
S
HN
N
OH
O
O
Br
OH
16
OH
Br

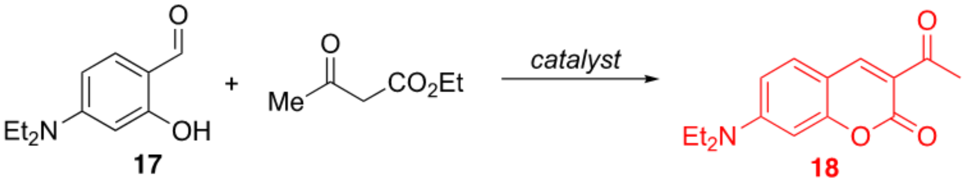
(p)



(q) It is an example of a Knoevenagel condensation.

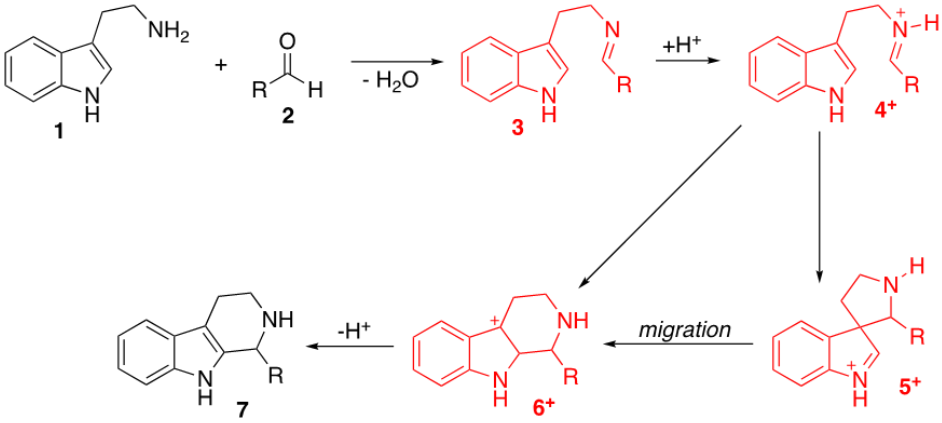


(r) Cyclisation is the reason why only one product is formed in this case.

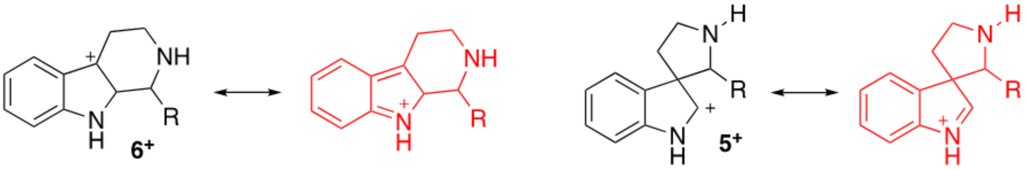


Answer - 12. Imine`s guide to the biochemical galaxy

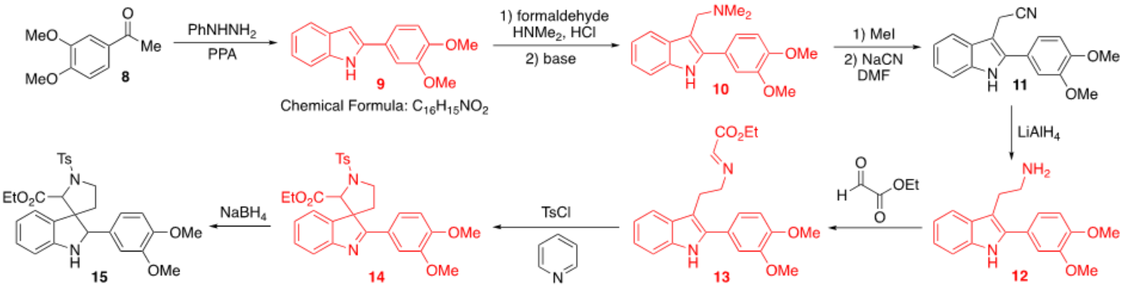
(a) Cations 4^+ and 5^+ are iminium salts discussed in the previous task.



(b)



(c)

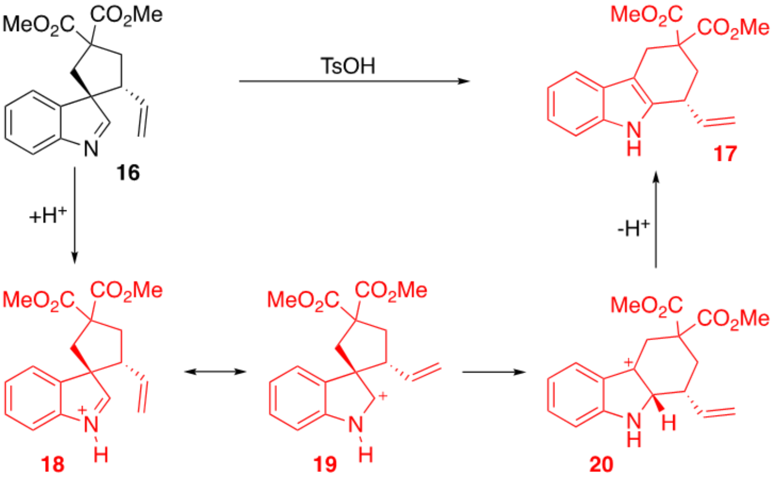


(d)

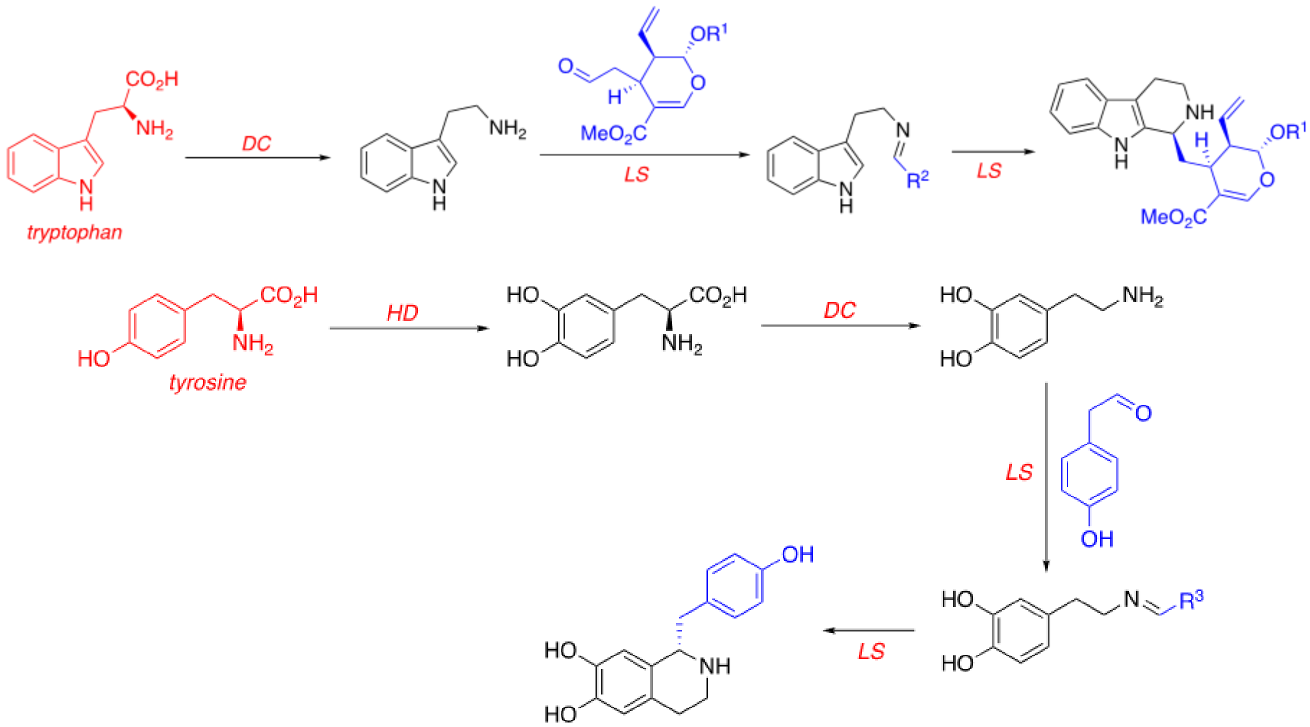
A. Aromatisation is favourable.
B. Aromatisation is unfavourable.
C. Aromatisation is possible.
D. Aromatisation is impossible.
E. Deprotonation is possible.
F. Deprotonation is impossible.
G. Steric hindrance enhances the rate of six-membered ring formation.
H. Steric hindrance decreases the rate of six-membered ring formation.

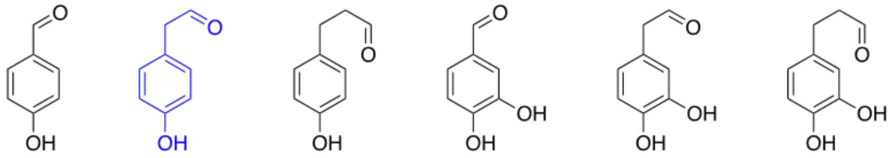
(e) Compound **15** has three stereocenters, which means 2^3 = **8** stereoisomers.

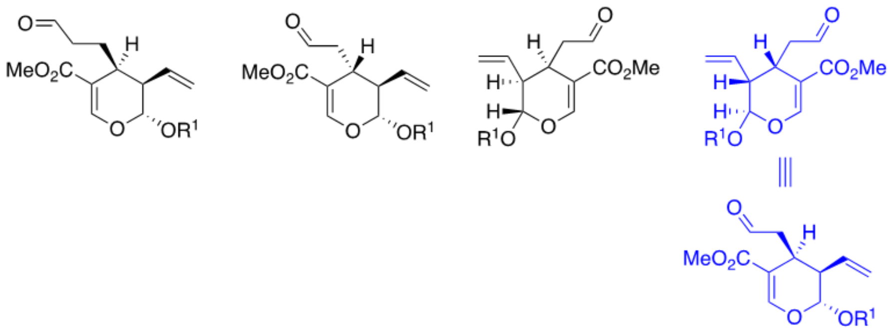
(f)



(g)


tryptophan
DC
LS
LS
MeO$_2$C
OR^1
R^2
tyrosine
HD
DC
LS
LS
R^3
HO
OH
NH$_2$
CO$_2$H
NH

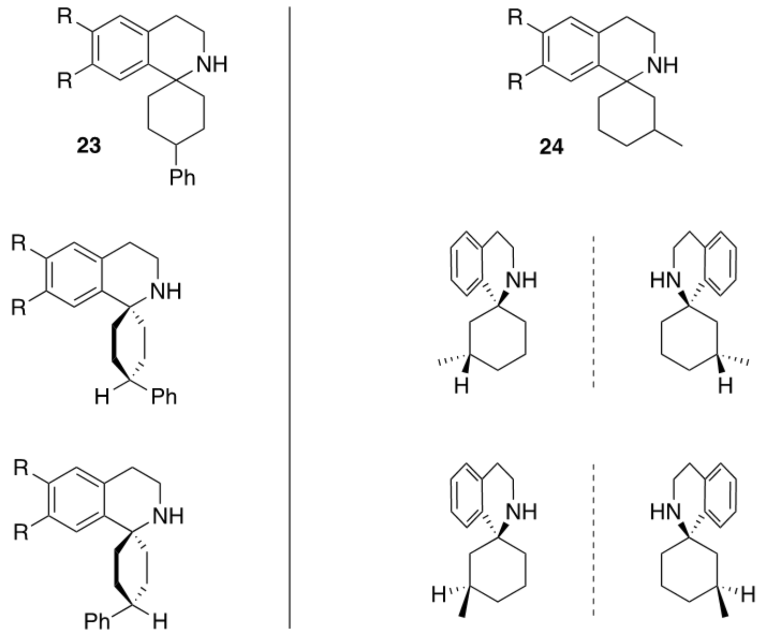

O
OH


O
H
MeO$_2$C
CO$_2$Me
OR^1
R^{1}O

(h) The number of stereoisomers for **23**: **2**

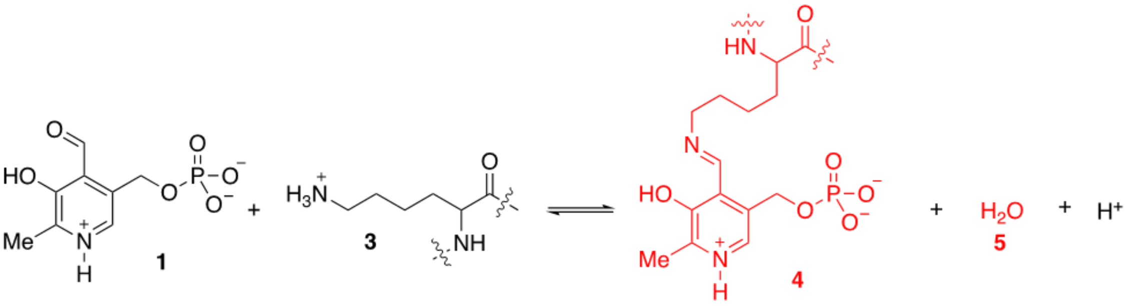
The number of stereoisomers for **24**: **4**

There are two achiral diastereomers for **23**. Compound **24** has two chiral diastereomers (i.e, two pairs of enantiomers or four stereoisomers in total).

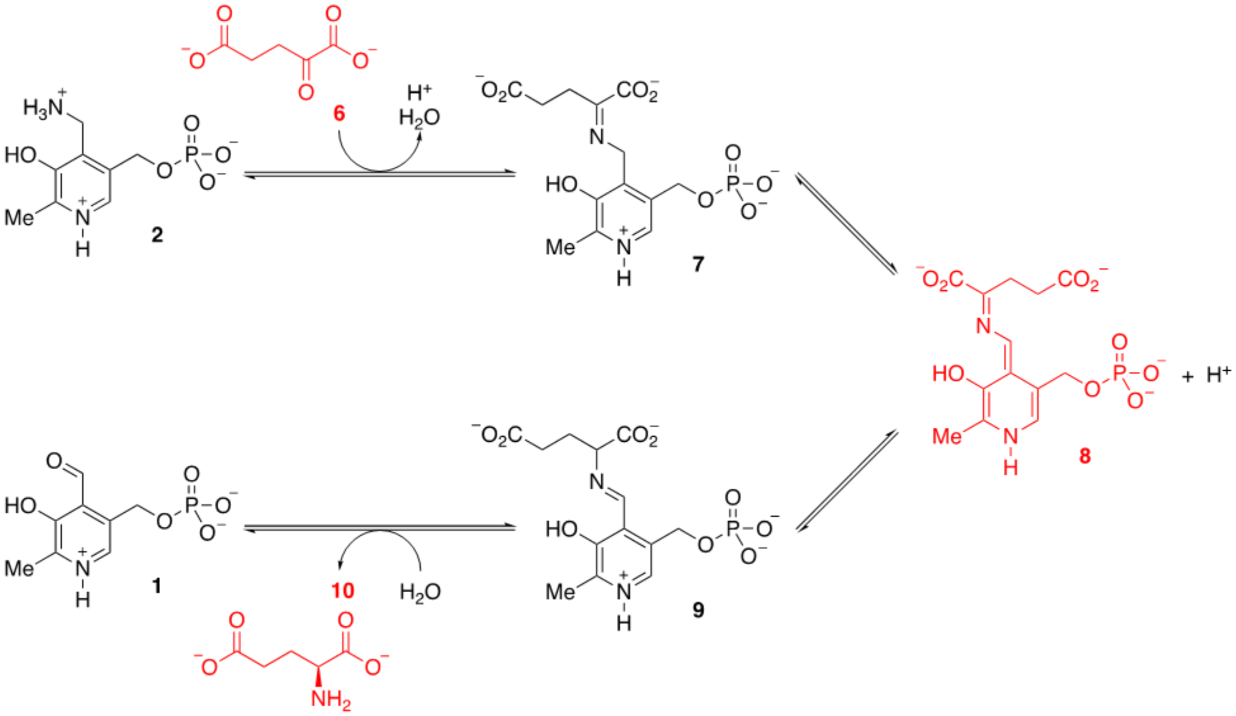


13. Schiff bases, the Universe, and biochemistry

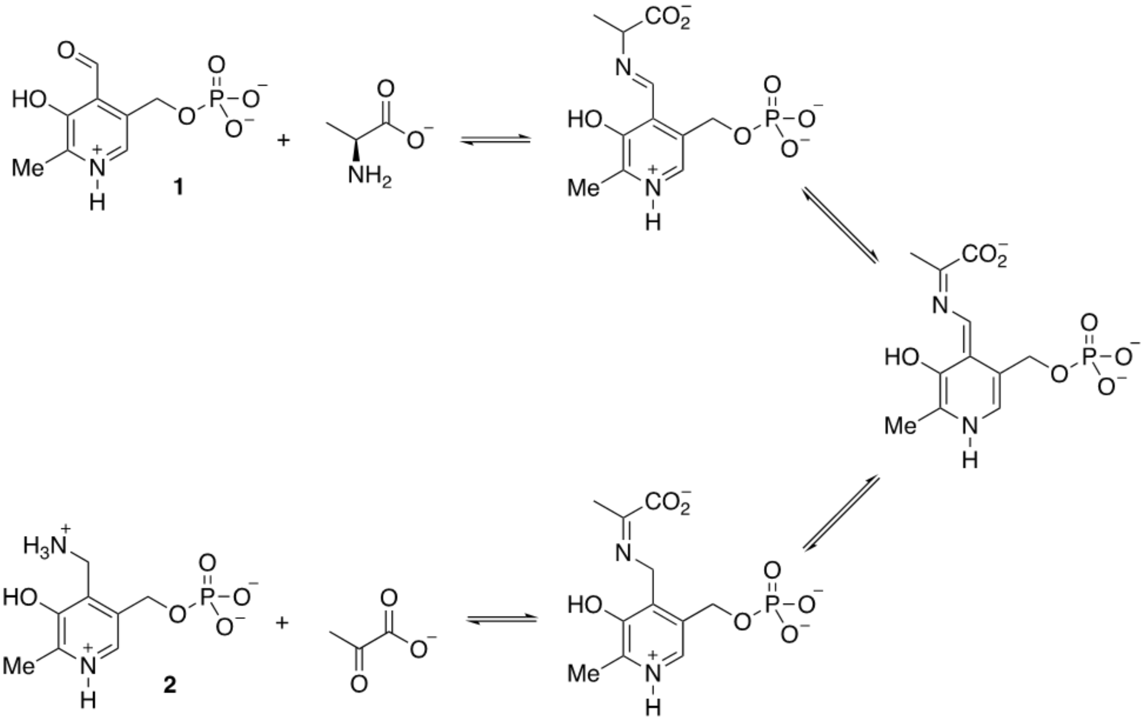
(a)



(b) E1 is alanine amino transferase or alanine transaminase (ALT).



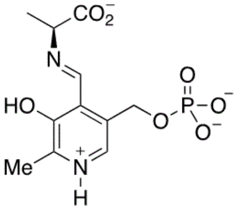
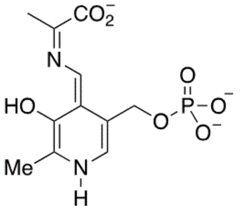
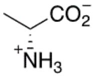
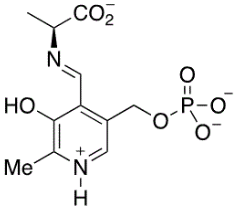
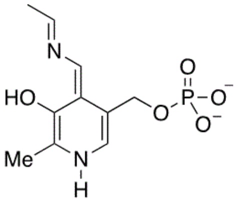
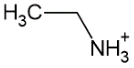
(c)



(d) (c) Being electron deficient, the pyridinium ring withdraws electron density from the α-carbon atom.

This leads to elimination of one of its substituents.

(e)

Reaction type	Initial Schiff base	Quinoid intermediate	Reaction product(s)
a)			 + PLP
b)			 + PLP

(f)

a) Alanine

b) Arginine

c) Asparagine

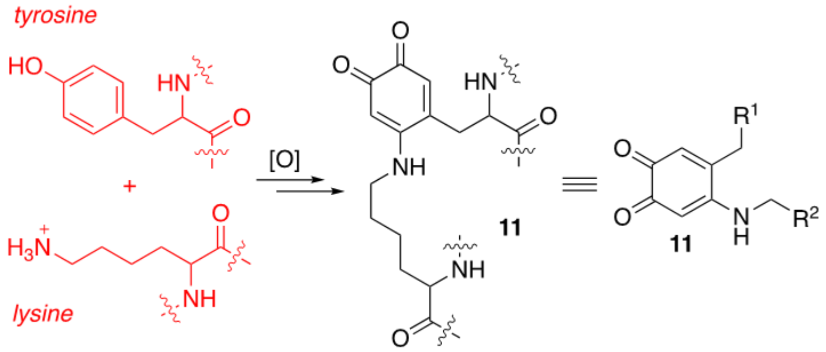
d) Glycine

e) Methionine

f) Tyrosine

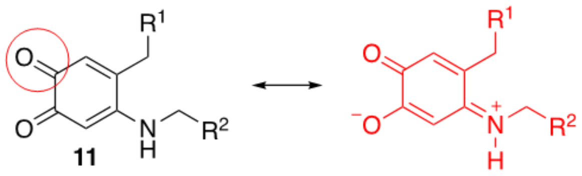
g) Tryptophan

h) Lysine

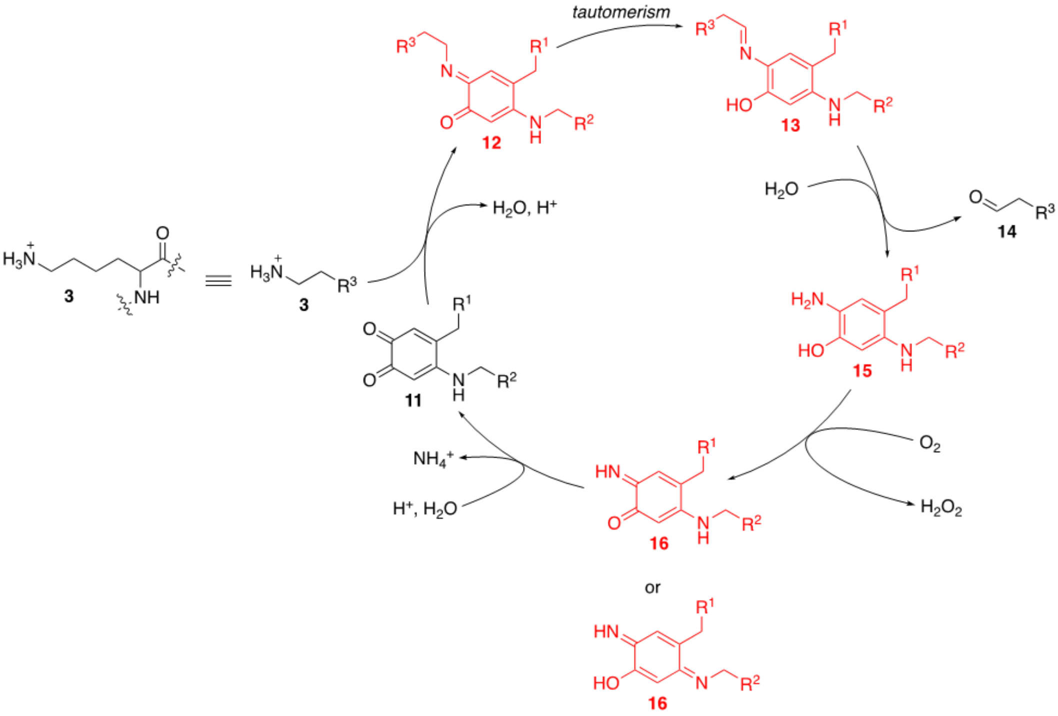


E_2 is lysyl oxidase (LOX).

(g)



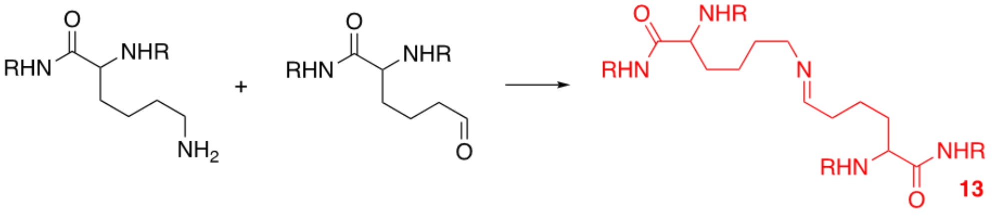
(h) **12** is the product of Schiff base formation between lysine residue **3** and the most reactive carbonyl group of the co-factor. Migration of the double bond with subsequent hydrolysis affords the allysine residue. The reduced form of the co-factor is oxidised, and then the imine is hydrolysed which terminates the cycle.



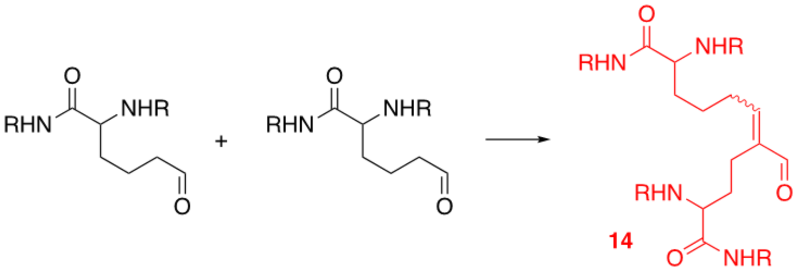
(i)

Spectrum number	Molecular ion $[M+H]^+$	Compound
1	145	
2	146	
3	147	regular lysine
4	148	22, 23, 25, 27, 28, 30, 31
5	149	24, 26, 29
6	150	

(j)

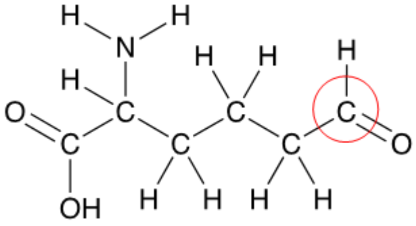


13

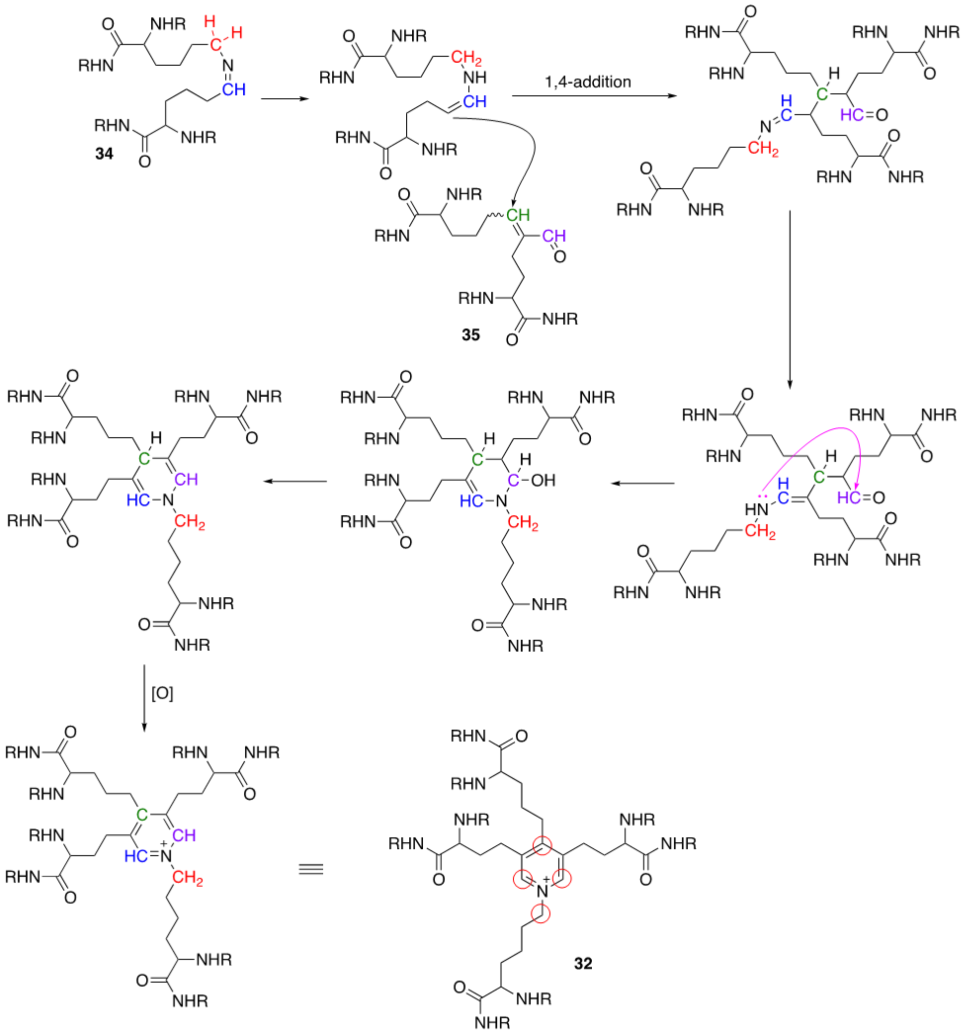


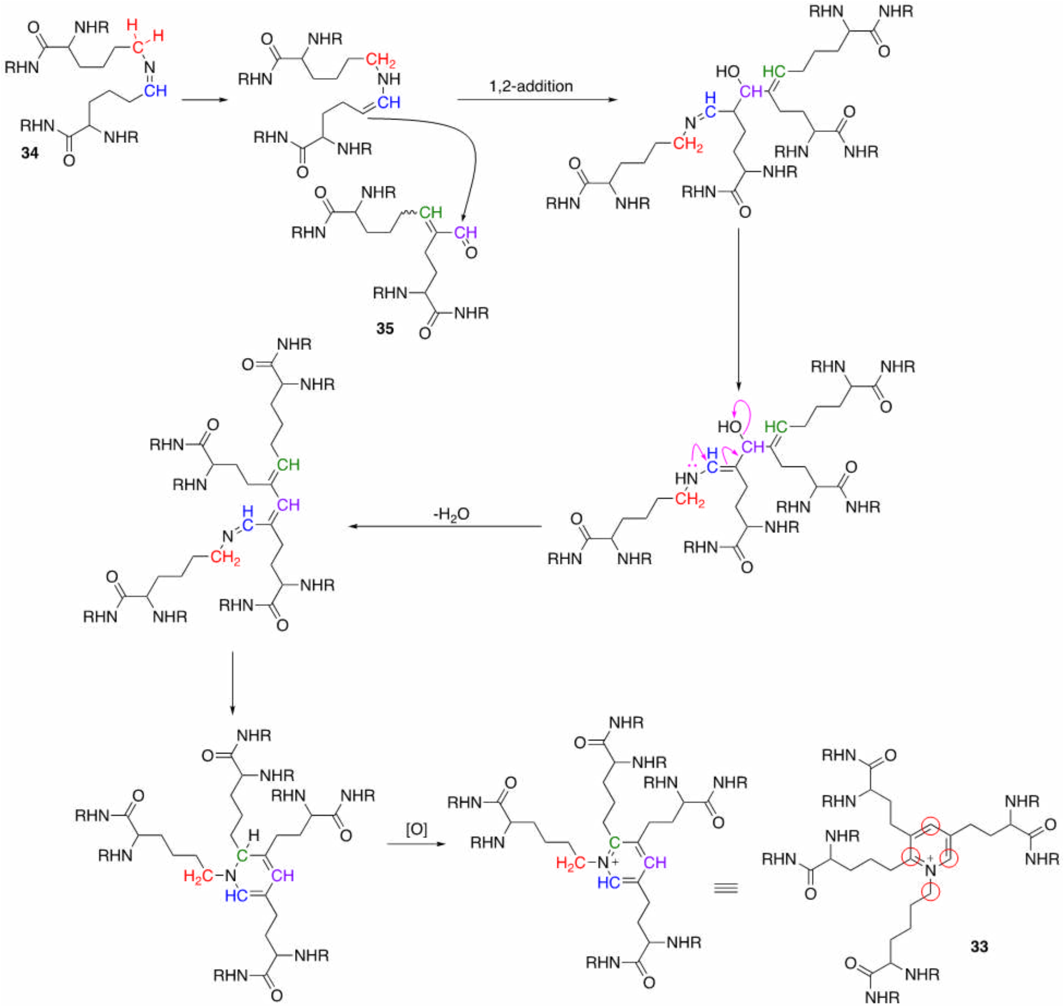
14

(k)



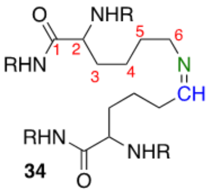
(l) There are several ways to assess this problem. The first option is to trace the carbon atoms in the ring formation mechanism as shown below.

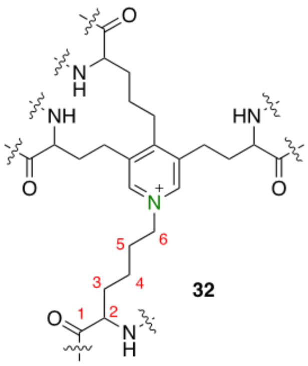


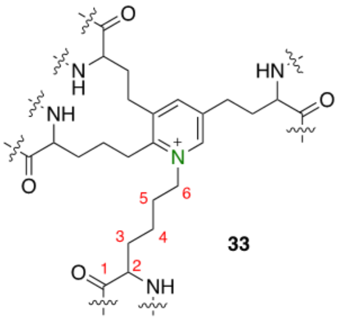


The second option is to know how to count to six. :)

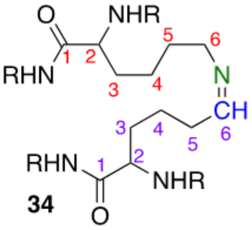
First find a lysine molecule, because there is only one, while there are three allysine molecules. The green nitrogen atom is easy to spot.


34

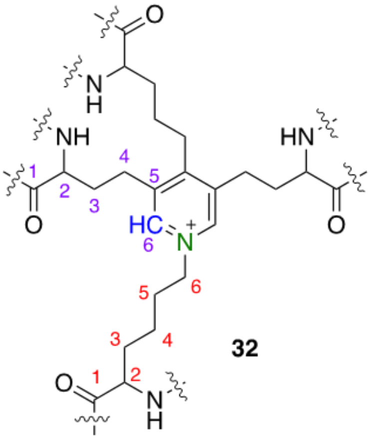

32


33

32 is a symmetrical compound. The first allysine is easy to spot by counting to six.

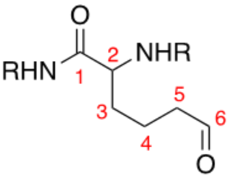


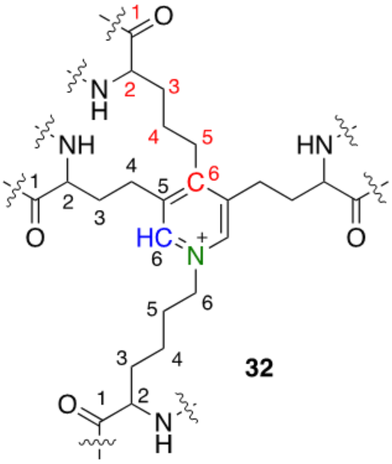
34



32

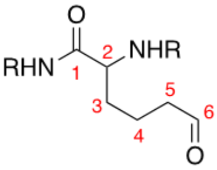
Subsequently, assigning the longer chain numbered in red is more straightforward.

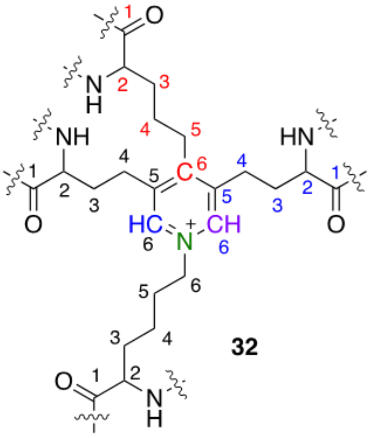




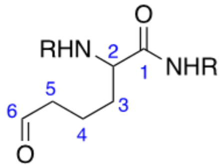
32

The last allysine is the six carbon atoms left without numbers.

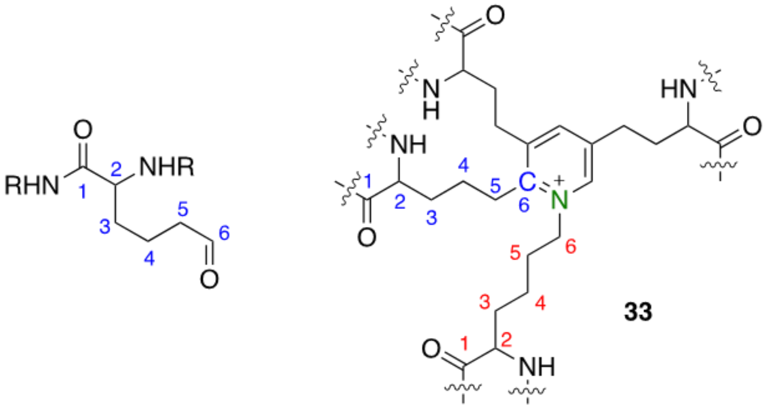




32

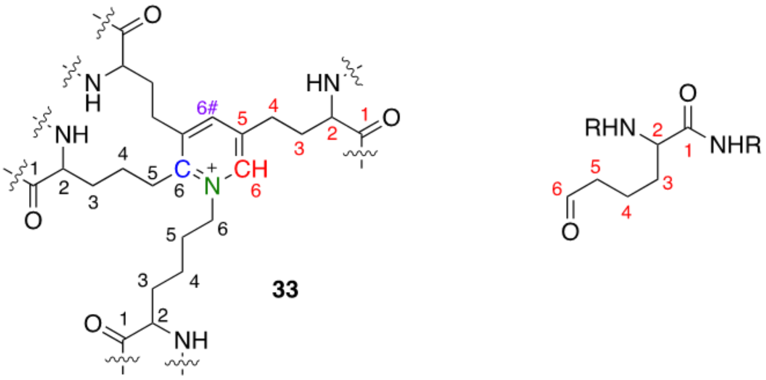


For compound **33**, it is simpler to compare it with allysine itself. The longest chain is found first.



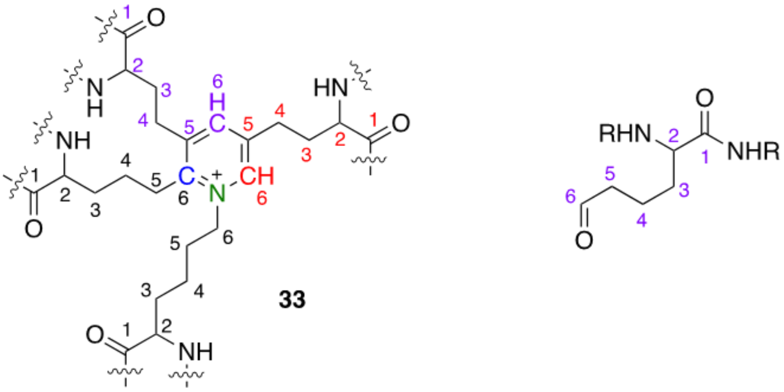
33

If the right chain is analysed, carbon 6 cannot be left out. When carbon atom #6 is included in this counting, red carbon 6 will have come out of “nowhere”, which is impossible.



33

The last allysine is the six carbon atoms left without numbers.



33

14. UAE's driving force

(a) The order of increasing boiling points:

2,2-dimethylbutane	dodecane	pentane-1-thiol	propene	pentan-1-ol	hexane	benzene
2	7	5	1	6	3	4

(b) **X** – S, **A** – H_2S, **B** – SO_2, **C** – S_8

The reaction: $16H_2S + 8SO_2 \rightarrow 3S_8 + 16H_2O$

(c) Sulfur has four stable isotopes: ^{32}S, ^{33}S, ^{34}S, ^{36}S.

Peak	256	257	258
I, %	70.40	4.76	25.17

S_8 with a mass of 256 is $^{32}S_8$. Therefore, the probability of this combination of isotopes is $0.9485^8 = 0.6551$ (65.51%).

S_8 with a mass of 257 is $^{32}S_7{}^{33}S$. Therefore, the probability of this combination of isotopes is $8{\cdot}0.9485^7{\cdot}x$, where x is the abundance of ^{33}S.

S_8 with a mass of 258 is either $^{32}S_6{}^{33}S_2$ or $^{32}S_7{}^{34}S$. Therefore, the probability of this combination of isotopes is $28{\cdot}0.9485^6{\cdot}x^2 + 8{\cdot}0.9485^7{\cdot}y$, where x is the abundance of ^{33}S and y is the abundance of ^{34}S.

The system of equations based on the ratio of intensities in the mass spectrum:

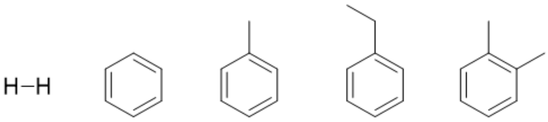
$$\begin{cases} \dfrac{70.40}{4.76} = \dfrac{0.9485^8}{8\cdot 0.9485^7\cdot x} = \dfrac{0.9485}{8\cdot x} \\ \dfrac{70.40}{25.17} = \dfrac{0.9485^8}{28\cdot 0.9485^6\cdot x^2 + 8\cdot 0.9485^7\cdot y} = \dfrac{0.9485^2}{28\cdot x^2 + 8\cdot 0.9485\cdot y} \end{cases} \Rightarrow \begin{cases} x = 0.0080\ (0.80\%) \\ y = 0.0422\ (4.22\%) \end{cases}$$

The total abundance of all four isotopes is 100%, therefore, the abundance of ^{36}S is:

$$1 - 0.9485 - 0.0080 - 0.0422 = 0.0013\ (0.13\%)$$

(d) There are 2 isomers of butane, 3 isomers of pentane and 5 isomers of hexane. In total, 10 compounds, including the initial linear alkanes (the isomerisation yield is unlikely to be 100%).

(e) Structures of the products (H_2 is also produced in addition to the aromatic compounds):

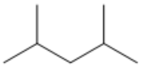


(f) $C_{16}H_{34}$ → hexadecane

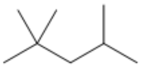
Cracking: $C_{16}H_{34} \rightarrow C_6H_{14} + 2C_5H_{10}$

Hydrocracking: $C_{16}H_{34} + H_2 \rightarrow 2C_8H_{18}$

(g) Structural formulae of **D** (2,4-dimethylpentane) and **E** (2,2,4-trimethylpentane):



D



E

(h) **Y** – Pb, **F** – $Pb(C_2H_5)_4$, **G** – C_2H_5Cl

The reaction: $4NaPb + 4C_2H_5Cl \rightarrow Pb(C_2H_5)_4 + 4NaCl + 3Pb$

15. In search of an oasis in the desert

(a) The degree of unsaturation of $C_5H_{10}O$ is $(5\cdot2 + 2 – 10)/2 = 1$. Therefore, there is either a double bond or a ring. The possible combinations are:

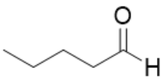
1) –CHO (aldehyde)
2) >C=O (ketone)
3) >C=C< (alkene) + –OH (alcohol)
4) >C=C< (alkene) + –O– (ether)
5) Cycloalkane (not typically considered as a functional group) + –OH (alcohol)
6) Cycloalkane (not typically considered as a functional group) + –O– (ether)
7) O-containing heterocycles (cyclic ethers): epoxide/oxetane/tetrahydrofuran

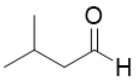
(b) Analysis of IR spectra allows us to determine the functional groups:

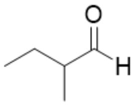
A, C, D, G, H: 1727–1728 cm^{-1} corresponds to aldehydes

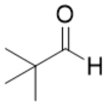
B, E, F: 1717–1720 cm^{-1} corresponds to ketones

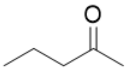
There are only four aldehydes and three ketones with the formula $C_5H_{10}O$:

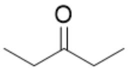


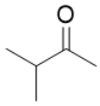




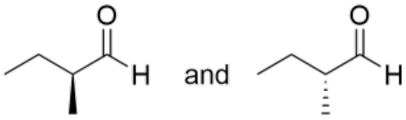






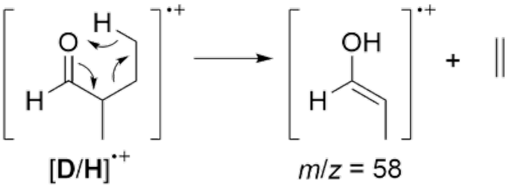


It seems like there should be one more aldehyde. However, if one carefully analyses the data, one can notice that **D** and **H** have absolutely the same data. This could be two enantiomers of the only chiral aldehyde $C_5H_{10}O$, 2-methylbutanal, which can’t be distinguished using IR spectroscopy and mass spectrometry:

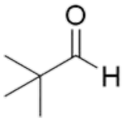


D/H

In their mass spectra, the strongest peaks are *m*/*z* 29, 41, 57, 58. The peak with *m*/*z* 29 is typical for the aldehydes as it corresponds to the HCO^+ produced in a bond cleavage. This peak can also be found in the mass spectra of all other aldehydes **A**, **C**, and **G**. The origin of peaks with *m*/*z* 41 (base peak) and 57 is presented in the solution to the next question. The peak with *m*/*z* 58 is due to McLafferty rearrangement:

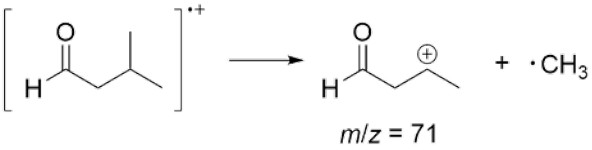


Analysing the structures of the three aldehydes left, one can notice that pentanal and 3-methylbutanal can undergo the McLafferty rearrangement giving the enol radical cation with *m*/*z* 44, while 2,2-dimethylpropanal can't. Both mass spectra of **A** and **C** have intense peaks with *m*/*z* 44, while the mass spectrum of **G** doesn't. Therefore, **G** is 2,2-dimethylpropanal and the peak with *m*/*z* 57 could be assigned to the *tert*-butyl cation (see the answer to the next question for the fragmentation scheme):

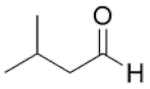


G

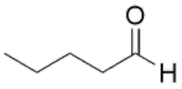
The noticeable difference between the mass spectra of **A** and **C** is the intensity of the peak with *m*/*z* 71, which is due to the loss of a methyl group from the molecular ion (86 – 15 = 71). In **A**, this peak is of significant intensity, which is more likely for the branched isomer 3-methylbutanal rather than linear pentanal due to the higher stability of the secondary carbocation rather than the primary:



Therefore, the structures of **A** and **C** are the following:

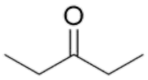


A



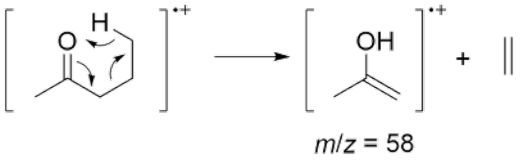
C

The remaining unknowns are the ketones **B**, **E**, and **F**. The main fragmentation pathway for ketones is bond cleavage producing an acyl cation. In the mass spectra of **B** and **F**, it is CH_3CO^+ (*m*/*z* 43), while in **E** it is $C_2H_5CO^+$ (*m*/*z* 57). Therefore, **E** is pentan-3-one (see the answer to the next question for the fragmentation scheme):

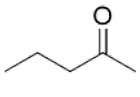


E

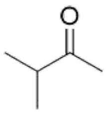
To differentiate between pentan-2-one and 3-methylbut-2-one, that both produce the acyl cation CH_3CO^+, one can notice that only pentan-2-one has a long enough chain to undergo the McLafferty rearrangement producing the enol radical cation with *m*/*z* 58:



This peak is only found in the mass spectrum of **B**. Therefore, **B** is pentan-2-one and **F** is 3-methylbut-2-one:

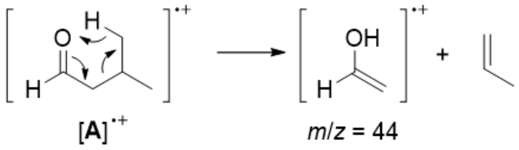


B

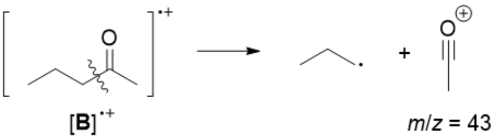


F

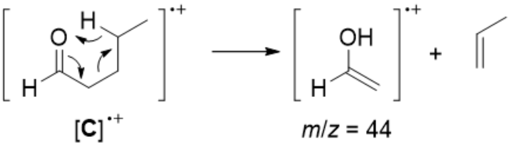
(c) Compound **A** – McLafferty rearrangement:



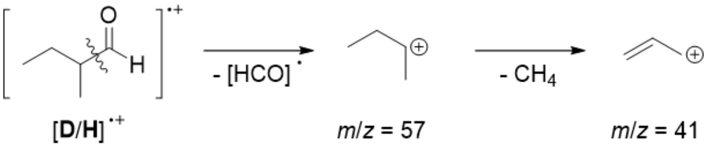
Compound **B** – bond cleavage with the formation of acyl cation (acyl radical has a lower ionisation energy than propyl radical):



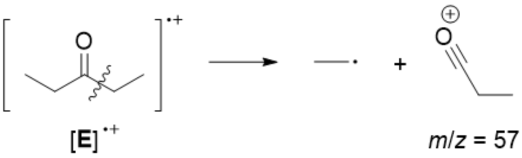
Compound **C** – McLafferty rearrangement:



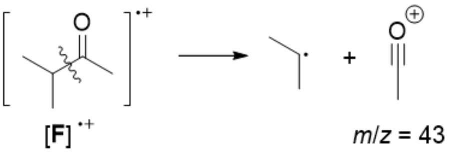
Enantiomers **D** and **H** – sequence of fragmentations forming the allyl cation, most likely:



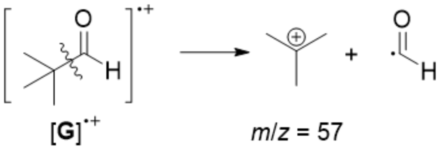
Compound **E** – bond cleavage with the formation of acyl cation (acyl radical has a lower ionisation energy than ethyl radical as can be seen from the relative intensities of the peaks with m/z 29 ($C_2H_5^+$) and 57 ($C_2H_5CO^+$)):



Compound **F** – bond cleavage with the formation of acyl cation (acyl radical has a lower ionisation energy than propyl radical):



Compound **G** – bond cleavage with the formation of *tert*-butyl cation (*tert*-butyl radical has a lower ionisation energy than formyl radical as can be seen from the relative intensities of the peaks with m/z 29 (HCO^+) and 57 (*t*-Bu^+)):



16. Fullerenes and polyhedra

(a) Each vertex connects to three edges. Each edge connects to two vertices. Therefore, there must be $\frac{3}{2}$ times the number of edges as the number of vertices. Hence, $e = \frac{3n}{2}$.

(b) The known values for *v* and *e* can be put into the Euler relationship.

$$\begin{gathered} v + f = e + 2 \\ n + f = \frac{3n}{2} + 2 \\ \boldsymbol{f = \frac{n}{2} + 2} \end{gathered}$$

(c) Pentagons have five vertices. Hexagons have six vertices. Each vertex is shared by three faces. Therefore, we can say that:

$$\frac{6h + 5p}{3} = v = n$$

We can also relate the number of pentagons and hexagons to the total number of faces and *n* via the Euler relationship:

$$f = p + h = \frac{n}{2} + 2$$

This gives a pair of simultaneous equations. We can then solve for *p* and *h*.

$$\begin{gathered} h = \frac{n}{2} + 2 - p \\ \frac{6\left(\frac{n}{2} + 2 - p\right) + 5p}{3} = n \\ \frac{3n + 12 - 6p + 5p}{3} = n \\ 3n + 12 - p = 3n \\ \boldsymbol{p = 12} \\ h = \frac{n}{2} + 2 - 12 \\ \boldsymbol{h = \frac{n}{2} - 10} \end{gathered}$$

(d) Dodecahedron. Students should recognise the dodecahedron as one of the five Platonic solids. All 12 faces are regular pentagons. Note that C_{20} is predicted as the smallest possible fullerene. Structures where two pentagons share an edge have increased bond angle strain and in C_{20} all edges are shared by two pentagons making it a very strained structure.

(e) These can be derived from the figures in the question and the equations.

(a,b)	*v = n*	*e*	*f*	*h*
(1,1)	60	90	32	20

(f) These can be derived from the figures in the question and the equations.

(a,b)	*v = n*	*e*	*f*	*h*
(2,0)	80	120	42	30
(2,1)	140	210	72	60
(2,2)	240	360	122	110
(3,0)	180	270	92	80
(3,2)	380	570	192	180

(g) Structure (i) (4,0). Structure (ii) (3,3). Structure (iii) (6,6). Structure (iv) (3,1). Structure (v) (4,3). Structure (vi) (10,6).

These Goldberg polyhedra fall into three classes. The first class can be described as (*a*,0), i.e., where one of *a* or *b* is zero. These structures have planes of symmetry and are achiral. This means that (4,0) and (0,4) are equivalent. Hence, (0,4) should also be considered a correct answer for structure (i). The convention is for *b* to be zero in these structures. The second class can be described as *a* = *b*. These structures also possess planes of symmetry and are achiral. The third class are the remaining structures where *a* and *b* are not equal and are both non-zero. These structures do not possess mirror planes and are chiral structures. This means that (3,1) and (1,3) are not the same and are in fact mirror images (enantiomers) of each other. For structures (iv), (v), and (vi) either permutation of numbers can be accepted as *a* and *b* directions have not been specified here. However, it is important to realise that these are different.

(h) (i): The structures (6,0) and (7,0) have different numbers of faces, 362 and 492 faces respectively. The only descriptor that applies here is allotropes.
(ii): The structures (7,0) and (5,3) have the same number of faces (492) and therefore the same number of carbon atoms. They are both allotropes of each other and isomers of each other. They have different connectivity of pentagons and hexagons and so are not stereoisomers.
(iii) Structures (7,0) and (0,7) are exactly the same. A simple rotation converts one into the other. By convention the structure is called (7,0). This structure is achiral as the shape contains planes of symmetry.
(iv) Structures (5,3) and (3,5) are not the same. These structures are enantiomers of each other. These structures do not have mirror planes and are chiral. In addition to being enantiomers of each other, they also fall into the more general class of allotropes, isomers, and stereoisomers.

(i) To determine the relative intensity of peaks we need to consider a statistical factor in addition to just multiplying the abundances together. In $^{12}C_{60}$ there is only one possible arrangement, so this has a statistical factor of 1. In $^{12}C_{59}{}^{13}C$ there are 60 possible arrangements as each one of the carbons could be the ^{13}C, giving this a weighting of 60. In general, these weightings are given by the mathematical combination function (also known as the binomial distribution or Pascal's triangle). They can be determined from the following equation, for a species with n carbons of formula $^{12}C_x{}^{13}C_y$:

$$weighting = \frac{n!}{y!\,(n-y)!}$$

Amount of $^{12}C_{60} = (0.9894)^{60} = 52.761\%$
Amount of $^{12}C_{59}{}^{13}C = 60 \times (0.9894)^{59} \times (0.0106) = 33.916\%$
Ratio = 52.761:33.916 = 1.556:1

(j)

Amount of $^{12}C_{70} = (0.9894)^{70} = 47.428\%$
Amount of $^{12}C_{69}{}^{13}C = 70 \times (0.9894)^{69} \times (0.0106) = 35.568\%$
Ratio = 47.428:35.568 = 1.333:1

(k) For a structure where there are *n* ^{12}C carbon atoms the statistical weighting is:

$$\frac{n!}{0!\,(n-0)!} = 1$$

For a structure where there is one ^{13}C and the rest are ^{12}C the statistical weighting is:

$$\frac{n!}{1!\,(n-1)!} = n$$

For there to be a greater proportion of fullerenes with one ^{13}C than no ^{13}C, we therefore need:

$$\begin{gathered} n \times (0.9894)^{n-1} \times (0.0106) > (0.9894)^{n} \\ n > \frac{0.9894}{0.0106} \\ n > 93.3 \\ \boldsymbol{n = 94} \end{gathered}$$

Remember that fullerenes must have an even number of carbon atoms.

(l) For a structure where there are two ^{13}C and the rest are ^{12}C the statistical weighting is:

$$\frac{n!}{2!\,(n-2)!} = \frac{n(n-1)}{2}$$

For there to be a greater proportion of fullerenes with two ^{13}C than one ^{13}C, we therefore need:

$$\begin{gathered} \frac{n(n-1)}{2} \times (0.9894)^{n-2} \times (0.0106)^{2} > n \times (0.9894)^{n-1} \times (0.0106) \\ \frac{(n-1)}{2} \times (0.0106) > (0.9894) \\ n-1 > \frac{2 \times (0.9894)}{(0.0106)} \\ n > \frac{2 \times (0.9894)}{(0.0106)} + 1 \\ n > 187.7 \\ \boldsymbol{n = 188} \end{gathered}$$

Remember that fullerenes must have an even number of carbon atoms.

17. Photocatalysis

(a) H_2O splitting:

photocathode: $2H^+ + 2e \rightarrow H_2$

photoanode: $H_2O - 2e \rightarrow {}^1/_2O_2 + 2H^+$

(or $H_2O \rightarrow {}^1/_2O_2 + 2H^+ + 2e$)

overall: $H_2O \rightarrow H_2 + {}^1/_2O_2$

CO_2 methanation:

photocathode: $CO_2 + 8H^+ + 8e \rightarrow CH_4 + 2H_2O$

photoanode: $H_2O - 2e \rightarrow {}^1/_2O_2 + 2H^+$

(or $H_2O \rightarrow {}^1/_2O_2 + 2H^+ + 2e$)

overall: $CO_2 + 2H_2O \rightarrow CH_4 + 2O_2$

(b)

Electrochemical property	will change	will not change
Overall reaction		☑
Cathode potential	☑	
Emf		☑

(c)

i) The hole in the VB must be a stronger oxidant than oxygen, that is, lie below the level of 1.23 V and have a larger potential than 1.23 V, to be able to oxidise water to O_2. This is true for all semiconductors except Si and Cu_2O.

ii) To reduce water (H^+ at pH 0) to hydrogen, the electron in the CB must be a stronger reductant than H_2, that is, have a more negative potential that the potential for the H^+/H_2 redox couple (0.00 V). The edge of the CB must lie above the line E° = 0 V. This is true for all semiconductors except Fe_2O_3 and WO_3.

iii) Same as in b), but the potential must be below 0.17 V and the edge of the CB must lie above the line 0.17 V. Semiconductors: all except Fe_2O_3 and WO_3.

iv) The edge of the VB must be below 1.23 V and the edge of the CB above zero (the potential is negative). Semiconductors: TiO_2, ZnO, CdS, ZnS, and SiC.

(d) Take the interval to be 1 hour. The number of moles of incident photons:

$$n(h\nu) = \frac{E}{E_m} = \frac{Pt}{\frac{hcN_A}{\lambda}} = \frac{200 \cdot 10^{-3}\ \mathrm{J \cdot s^{-1}} \cdot 3600\ \mathrm{s}}{\frac{\left(6.63 \cdot 10^{-34}\ \mathrm{J \cdot s}\right) \cdot \left(3.00 \cdot 10^{8}\ \mathrm{m \cdot s^{1}}\right) \cdot \left(6.02 \cdot 10^{23}\ \mathrm{mol^{-1}}\right)}{532 \cdot 10^{-9}\ \mathrm{m}}} =$$

$$= 3.2 \cdot 10^{-3}\ \mathrm{mol}$$

The number of moles of H_2:

$$n(\mathrm{H_2}) = 160 \cdot 10^{-6}\ \mathrm{mol{\cdot}h^{-1}g^{-1}} \cdot 1\ \mathrm{h} \cdot 0.1\ \mathrm{g} = 1.6{\cdot}10^{-5}\ \mathrm{mol.}$$

Formation of one H_2 molecule requires two electrons, hence,

$$n(e) = 1.6 \cdot 10^{-5}\ \mathrm{mol} \cdot 2 = 3.2{\cdot}10^{-5}\ \mathrm{mol.}$$

Apparent quantum yield:

$$\mathrm{AQY} = \frac{3.2{\cdot}10^{-5}\ \mathrm{mol}}{3.2{\cdot}10^{-3}\ \mathrm{mol}} \cdot 100\% = 1\%.$$

Compared to the early photocatalytic experiments, the AQY is not bad!

18. Semiconductors

(a) CdTe consists of cadmium (Cd) and tellurium (Te), where Cd belongs to Group 12 and Te belongs to Group 16. The Cd atoms provide 5s and 5p orbitals, while the Te atoms contribute 5p orbitals. These orbitals combine to form the molecular orbitals of the crystal structure.

- The valence band of CdTe is primarily formed from the overlap of Te 5p orbitals. These are bonding orbitals, and they are filled with electrons.
- The conduction band is formed from the Cd 5s and 5p orbitals. These orbitals are higher in energy and remain unfilled in the absence of external energy (such as photons).

When light of sufficient energy (greater than the band gap) is absorbed, electrons are excited from the valence band to the conduction band, creating electron-hole pairs that are crucial for photovoltaic action.

(b) The energy of the band gap in CdTe is 1.45 eV. First, convert this energy to joules:

$$E_\mathrm{g} = 1.45\ \mathrm{eV}\ \times\ 1.602\ \times\ 10^{-19}\,\mathrm{C} = 2.323\ \times\ 10^{-19}\,\mathrm{J}$$

Then, calculate the cuttoff wavelength:

$$\lambda_{cutoff} = \frac{6.626 \times 10^{-34}\,\mathrm{J\,s} \times 2.998 \times 10^{8}\,\mathrm{m\,s^{-1}}}{2.323 \times 10^{-19}\,\mathrm{J}} = 8.55\ \times\ 10^{-7}\ \mathrm{m}\ =\ 855\ \mathrm{nm}$$

The cutoff wavelength of CdTe is approximately 855 nm. This means that CdTe absorbs light with wavelengths shorter than 855 nm and is transparent to light with longer wavelengths.

(c) The UAE experiences intense sunlight with a peak at around 550 nm (green-yellow light). The band gap of CdTe (1.45 eV) corresponds to 855 nm, meaning it absorbs light from the UV and visible parts of the spectrum effectively, especially the shorter wavelengths where the solar intensity is strong. This makes CdTe an efficient material for capturing a significant proportion of the sunlight available in the UAE.

(d) The optical absorption coefficient at 500 nm is $2 \times 10^5\,\mathrm{cm^{-1}}$. The penetration depth *d* is the inverse of the absorption coefficient:

$$d\ =\ \frac{1}{\alpha}\ =\ \frac{1}{2 \times 10^{5}\ \mathrm{cm^{-1}}}\ =\ 5\ \times\ 10^{-6}\ \mathrm{cm}\ =\ 50\ \mathrm{nm}$$

This means that light at 500 nm penetrates only about 50 nm into the CdTe before it is absorbed.

(e) The shallow penetration depth indicates that CdTe can absorb sunlight efficiently in a very thin layer. This property is advantageous for creating thin-film solar cells, which require less material and can be manufactured at a lower cost. In the UAE, where space for large solar installations is abundant, CdTe's efficient light absorption makes it an ideal candidate for large-scale solar energy production.

(f) In bulk CdSe, the valence band is primarily formed from the Se 4p orbitals, and the conduction band is formed from the Cd 5s orbitals. The energy difference between the top of the valence band and the bottom of the conduction band defines the band gap. In quantum dots, due to the small size of the particles, the electron and hole wavefunctions are spatially confined. This confinement increases the energy of the electronic states, effectively widening the band gap.

(g) As the size of the QD decreases, the quantum confinement effect becomes stronger, increasing the band gap. Smaller QDs absorb higher energy (shorter wavelength) photons, while larger QDs absorb lower energy (longer wavelength) photons. This tunability is advantageous in solar cells because different sized QDs can be used to capture different parts of the solar spectrum. This adaptability is particularly useful in the UAE, where sunlight is abundant across the visible and near-infrared spectrum.

(h) Using this mass approximation formula:

$$\boldsymbol{E_g(R) = E_g^{\infty} + \frac{h^2}{8R^2}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right) - \frac{1.8e^2}{4\pi\varepsilon_0\varepsilon R}}$$

We can calculate the kinetic energy term first,

$$\frac{h^2}{8R^2}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right) = \frac{(6.626\,x\,10^{-34})^2}{8(2.5\,x\,10^{-9})^2}\left(\frac{1}{0.13\,x\,9.109\,x\,10^{-31}} + \frac{1}{0.45\,x\,9.109\,x\,10^{-31}}\right) \approx \boldsymbol{0.6\,eV}$$

Then, the Coulomb energy term,

$$\frac{1.8e^2}{4\pi\varepsilon_0\varepsilon R} = \frac{1.8\,x\,\left(1.602\,x\,10^{-19}\right)^2}{4\pi\,x\,8.85\,x\,10^{-12}\,x\,10\,x\,2.5\,x\,10^{-9}} \approx \boldsymbol{0.10\,eV}$$

Thus, the total band gap is:

$$\boldsymbol{E_g(R)} = 1.74\,eV + 0.6\,eV - 0.10\,eV = \boldsymbol{2.24\,eV}$$

(i) The bulk band gap of CdSe is 1.74 eV. For a quantum dot of 2.5 nm radius, the band gap is 2.36 eV, which is significantly higher due to quantum confinement. This shift indicates that smaller QDs absorb higher energy (shorter wavelength) light compared to bulk CdSe.

(j)

$$\lambda_{cutoff} = \frac{6.626 \times 10^{-34}\,\mathrm{J\,s} \times 2.998 \times 10^{8}\,\mathrm{m\,s^{-1}}}{2.36\ \mathrm{eV}\ \times 1.602 \times 10^{-19}\,\mathrm{J}} = 555\ \mathrm{nm}$$

(k) The absorption wavelength of 525 nm falls near the peak of the solar spectrum (~550 nm), making 2.5 nm CdSe QDs ideal for capturing solar energy in the UAE. This size of QD can efficiently absorb green light, which is a major component of the UAE’s intense sunlight.

(l) The radius of the QD (2.5 nm) is smaller than the exciton Bohr radius of CdSe (5.6 nm). This indicates that the QDs are in the strong quantum confinement regime, where both the electron and hole are spatially confined, significantly altering the energy levels and increasing the band gap.

(m) In the strong confinement regime, the energy levels are quantised, leading to a larger band gap. This makes QDs highly tunable for specific optical properties. The ability to control the band gap by simply changing the size of the QDs allows for the design of solar cells that can absorb a wide range of wavelengths, improving efficiency under the UAE's sunlight.

(n) To cover the visible spectrum (400-700 nm), we can use the absorption wavelength formula:

$$\lambda_{cutoff} = \frac{hc}{E_{\mathrm{g}}(R)}$$

Using the bulk band gap as a lower bound (E_g = 1.74 eV) for 700 nm light, R = 1.56 nm, and using the previously calculated band gap for 555 nm light, we know that a QD radius of 2.5 nm captures this wavelength. For 400 nm light, corresponding to 7.62 eV, we need a QD radius of approximately between 1.56 nm and 7.63 nm can absorb the entire visible spectrum.

(o) Quantum dots allow for precise tuning of the solar cell's absorption profile by varying their size, making them adaptable to the wide range of wavelengths in the UAE's sunlight. Furthermore, QDs can be easily integrated into flexible and lightweight devices, which is crucial for large-scale solar installations in desert environments where efficiency, adaptability, and durability are essential.

19. Reverse combustion

(a) CO_2 methanation:

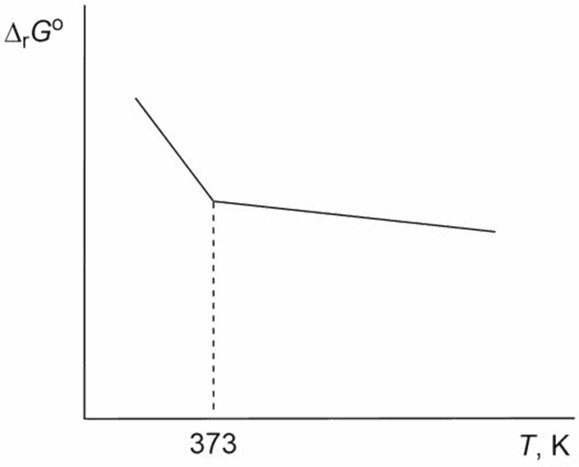
$$298\text{-}373\text{ K:}\quad CO_{2(g)} + 2H_2O_{(l)} \rightarrow CH_{4(g)} + 2O_{2(g)}$$

$$\Delta_r S^o = \frac{\Delta_r H^o - \Delta_r G^o}{T} = \frac{890000-818000}{298} = 241.6\ \frac{J}{\text{mol·K}}$$

$$373\text{-}800\text{ K:}\quad CO_{2(g)} + 2H_2O_{(g)} \rightarrow CH_{4(g)} + 2O_{2(g)}$$

$$\Delta_r S^o = 241.6 - 2 \cdot 118 = 5.6\ \frac{J}{\text{mol·K}}$$

The graph $\Delta_r G^\circ(T)$ consists of two lines – one with a more negative slope (292-373 K), and one with a less negative slope (373-800 K).



(b) The most stable system is $CO_2 + 2H_2O$, we take its standard Gibbs energy as zero, then $G^o(CH_4+2O_2)$ = 818 kJ/mol.

Consider decomposition of liquid water:

$$2H_2O(l) = 2H_2(g) + O_2(g).$$

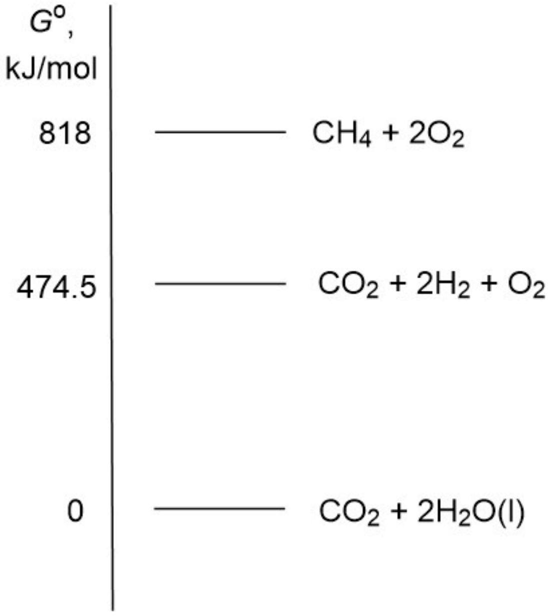
This reaction can be formally presented as a half-sum of two reactions:

$CO_2(g) + 2H_2O(l) \rightarrow CH_4(g) + 2O_2(g)$ $\qquad \Delta_r G^\circ_{298}$ = 818 kJ/mol,

$CH_4(g) + 2H_2O(l) \rightarrow CO_2(g) + 4H_2(g) \qquad \Delta_r G^\circ_{298} = 131$ kJ/mol.

The Gibbs energy for decomposition of 2 moles of $H_2O(l)$ is (818+131) / 2 = 474.5 kJ, then $G^o(CO_2+2H_2+O_2)$ = 474,5 kJ/mol.

The Gibbs energy diagram is as follows:



(c)

a) $CO_{2(g)} + 4H_{2(g)} \rightleftarrows CH_{4(g)} + 2H_2O_{(l)}$

$$\Delta_r S^o = \frac{\Delta_r H^o - \Delta_r G^o}{T} = \frac{-253000-(-131000)}{298} = -409.4\ \frac{\text{J}}{\text{mol·K}}$$

$$\Delta_r H^o = -253\ \frac{\text{kJ}}{\text{mol}}$$

$CO_{2(g)} + 4H_{2(g)} \rightleftarrows CH_{4(g)} + 2H_2O_{(g)}$

$$\Delta_r S^o = -409.4 + 2 \cdot 118 = -173.4\ \frac{\text{J}}{\text{mol·K}}$$

$$\Delta_r H^o = -253 + 2 \cdot 44 = -165\ \frac{\text{kJ}}{\text{mol}}$$

$$\Delta_r G^o_{773} = -165000 - 773 \cdot (-173.4) = -30960\ \frac{\text{J}}{\text{mol}}$$

$$K_p = \exp\left(\frac{30960}{8.314 \cdot 773}\right) = 124$$

(d)

	$n(CO_2)$, mol	$n(H_2)$, mol	$n(CH_4)$, mol	$n(H_2O)$, mol
Initial mixture	1	4	0	0
Reaction	-0.9	-3.6	0.9	1.8
Equilibrium mixture	0.1	0.4	0.9	1.8

Total: 3.2 moles in the equilibrium mixture.

$$K_p = \frac{x_{CH_4} x^2_{H_2O}}{x_{CO_2} x^4_{H_2} P^2} = \frac{\left(\frac{0.9}{3.2}\right)\left(\frac{1.8}{3.2}\right)^2}{\left(\frac{0.1}{3.2}\right)\left(\frac{0.4}{3.2}\right)^4 P^2} = 124$$

$P = 9.7$ bar.

(e) Energy of one mole of photons:

$$E_m = \frac{hcN_\mathrm{A}}{\lambda} = \frac{\left(6.63\cdot10^{-34}\ \mathrm{J\cdot s}\right)\cdot\left(3.00\cdot10^{8}\ \mathrm{m\cdot s^{1}}\right)\cdot\left(6.02\cdot10^{23}\ \mathrm{mol^{-1}}\right)}{420\cdot10^{-9}\ \mathrm{m}} = 285090\ \mathrm{J/mol}$$

The number of moles of photons:

$$n(h\nu) = \frac{n(\mathrm{CH_4})}{\mathrm{QY}} = \frac{0.0011}{0.0018} = 0.61\ \mathrm{mol}$$

Time of irradiation:

$$t = \frac{E}{P} = \frac{0.61\ \mathrm{mol}\ \cdot\ 285090\ \mathrm{J/mol}}{1.00\ \mathrm{J/s}} = 173900\ \mathrm{s} = 48\ \mathrm{h}$$

20. New drug formulation

(a) Freezing point depression is given by:

$$\Delta T_f = K_f \cdot m$$

Where:

- $\Delta T_f =$−15 °C − (−16.5 °C) = 1.5 °C (freezing point depression),
- $K_f =$4.5 K·kg·mol^{-1} (freezing point depression constant).

Rearrange the equation to solve for molality, *m*:

$$m = \frac{\Delta T_f}{K_f} = \frac{1.5}{4.5} = 0.333 \text{ mol } / \text{ kg}$$

So, the molality of the drug in the solution is 0.333 mol / kg.

(b) Molality, *m*, is defined as:

$$m = \frac{n_{\text{solute}}}{m_{\text{solvent}}}$$

Where:

- n_{solute} is the number of moles of the drug
- m_{solvent} is the mass of the solvent in kg

Given that m_{solvent} = 250 g = 0.250 kg, rearrange to solve for the number of moles:

$$n_{\text{solute}} = m \cdot m_{\text{solvent}} = 0.333 \frac{\text{mol}}{\text{kg}} \cdot 0.250 \text{ kg} = 0.0833 \text{ mol}$$

the molecular mass of the drug:

$$M_{\text{drug}} = \frac{\text{mass of the drug}}{n_{\text{solute}}} = \frac{15 \text{ g}}{0.0833 \text{ mol}} = 180 \text{ g/mol}$$

Thus, the molecular mass of the drug is approximately **180 g / mol.**

(c) We will use the Clausius-Clapeyron equation to estimate the new vapour pressure of the solvent after dissolving the drug.

The Clausius-Clapeyron equation is:

$$\ln\left(\frac{P_2}{P_1}\right) = -\frac{\Delta_{\text{vap}}H^{\text{o}}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Where:

- P_1 = 0.0075 atm, the vapour pressure at T_1 = −15 °C = 258.15 K,
- P_2 is the vapour pressure of the pure solvent at T_2,
- T_2 = 256.65 K (−16.5 °C),
- $\Delta_{vap}H^o$ = 25.0 kJ·mol^{-1} = 25000 J·mol^{-1},
- R = 8.314 J·mol^{-1}·K^{-1}.

Rearrange the equation:

$$\ln\left(\frac{P_2}{0.0075}\right) = -\frac{25000}{8.314}\left(\frac{1}{256.65} - \frac{1}{258.15}\right)$$

$$\ln\left(\frac{P_2}{0.0075}\right) = -0.0681$$

$$P_2 = 0.0075 \cdot e^{-0.0681} = 0.0070 \text{ atm}$$

The vapour pressure of the pure solvent at −16.5 °C is **0.0070 atm.**

With the drug dissolved, the vapour pressure decreases according to Raoult's law:

$$P_{\text{solution}} = x_{\text{solvent}} \cdot P_{\text{pure solvent at -16.5°C}}$$

Calculating the mole fraction of the solvent:

$$n_{\text{solvent}} = \frac{250 \text{ g}}{100 \text{ g/mol}} = 2.5 \text{ mol}$$

Moles of the solute: n_{solute} = 0.0833 mol

Then the mole fraction of the solvent is:

$$x_{\text{solvent}} = \frac{n_{\text{solvent}}}{n_{\text{solvent}} + n_{\text{solute}}} = \frac{2.5}{2.5 + 0.0833} = 0.968$$

The vapour pressure of the solvent is:

$$P_{\text{solution}} = 0.968 \cdot 0.0070 = 0.0068 \text{ atm}$$

Thus, the vapour pressure of the solvent at −16.5 °C is approximately **0.0068 atm.**

(d) The freezing point depression ensures that the drug remains in liquid form at lower temperatures, which is essential for maintaining stability during transport through colder areas in the UAE. The reduction in vapour pressure also minimises evaporation loss, which is crucial for both stability and maintaining the intended drug concentration. In high-altitude areas such as Jebel Hafeet, where temperatures can drop significantly at night, these adjustments enhance the drug's transport reliability and longevity under variable UAE climate conditions.

21. Cloud seeding

(a) If we take h = 10 km, the air pressure will be around 28 kPa, and we could check via the Clausius equation that the melting temperature variation is around 0.02 K from its initial value, which means that we can consider T_m as constant and that it does not depend on the pressure over this range. So, we just need to know at what height the temperature becomes $0\ ^{\circ}\mathrm{C}$.

$6.5\ h = 45$, so h = 6.92 km, and thus at this height ice clouds can be formed.

(b) As the clouds form at 12.9 km instead of 6.92 km, the supercooling temperature is $T_{sc} = (6.92 - 12.9) \cdot 6.5 = -38.8\ {}^{o}C$.

(c) Using a Born-Haber cycle, we obtain

$$\Delta_f H^0(AgI) = \Delta_{sub} H^0(Ag) + 0.5\ \Delta_{sub}\ H^0(I_2) + 0.5\ \Delta_{diss}\ H^0(I_2) + \Delta_{Aff} H^0(I) + \Delta_{Ion} H^0(Ag) + \Delta_{lattice} H^0(AgI)$$

$$\Delta_{f,lattice} H^0(AgI) = \Delta_f H^0(AgI) - \Delta_{sub} H^0(Ag) - 0.5\ \Delta_{sub}\ H^0(I_2) - 0.5\ \Delta_{diss}\ H^0(I_2) - \Delta_{Aff} H^0(I) - \Delta_{Ion} H^0(Ag)$$

$$\Delta_{f,lattice} H^0(AgI) = -62 - 285 - 0.5 \cdot 57 - 0.5 \cdot 150 - (-295) - 731 = -886.5\ \mathrm{kJ}\ /\ \mathrm{mol}$$

(d) The numerator is the same ($16\pi\gamma_{iw}^3$) for both calculations as this parameter is determined by the water, so we can cancel it out and can directly calculate the ratio between $\mathit{\Delta} G_{cl}(NaCl)$ and $\mathit{\Delta} G_{cl}(AgI)$:

$$\frac{\mathit{\Delta} G_{cl}(NaCl)}{\mathit{\Delta} G_{cl}(AgI)} = \frac{3(\mathit{\Delta} G_v(AgI)+\mathit{\Delta} G_{sl}(AgI))^2}{3(\mathit{\Delta} G_v(NaCl)+\mathit{\Delta} G_{sl}(NaCl))^2}$$

$$\frac{108300}{\mathit{\Delta} G_{cl}(AgI)} = \frac{3\left(6030\cdot\frac{-6}{273}+0.001\cdot(-886500)\right)^2}{3\left(6030\cdot\frac{-10}{273}-350\right)^2} = 3.19$$

$$\mathit{\Delta} G_{cl}(AgCl)\ =\ 33.9\ \mathrm{kJ}\,/\,\mathrm{mol}$$

(e) B) above the desert.

This occurs in regions where less nucleation is possible, so in the desert on a calm day. (Above the sea NaCl is the nucleation agent).

(f) The ion number on the surface is

$$N_S = \frac{4\pi R^2}{4\pi r^2} \cdot 0.8$$

The ion numbers in the particle is

$$N_V = \frac{\frac{4}{3}\pi R^3}{\frac{4}{3}\pi r^3} \cdot 0.7$$

where r- is ion radius and R is nanoparticle radius.

$$\frac{N_S}{N_V} = \frac{r}{R} \cdot \frac{0.8}{0.7} = \frac{0.3}{R} \cdot \frac{0.8}{0.7} = 0.00342$$

(g) From the graph we observe that the mass fraction of 75 nm nanoparticles is the same in both cases, so the mass of the second sample is also 1.08 g.

The difference between the samples is in the total surface area, as both size distributions are different.

(h) In this type of kinetics, the concentration is not the main parameter to find the order, but rather it is the total surface area which has the most influence.

Firstly, we need to distinguish different particle sizes using the mass fraction (α). Having more particles of a smaller size and mass will give a bigger surface area overall, so there is an inverse proportionality between rate and particle size.

The water does not affect the kinetics as it is in excess, so rate equation should be:

$$v = k[AgI]^n$$

where rate constant, *k,* is not a real constant as it depends on the particle distribution.

So *k* is composed of a term for each particle size.

$$k = \frac{k\prime}{r_1}\alpha_1^n + \frac{k\prime}{r_2}\alpha_2^n + \frac{k\prime}{r_3}\alpha_3^n + \frac{k\prime}{r_4}\alpha_4^n$$

We can write out the ratio of rates and could check proposed orders 0 and 1.

$$\frac{v_1}{v_2} = \frac{\frac{\alpha_{11}^n}{r_1} + \frac{\alpha_{12}^n}{r_2} + \frac{\alpha_{13}^n}{r_3} + \frac{\alpha_{14}^n}{r_4}}{\frac{\alpha_{21}^n}{r_1} + \frac{\alpha_{22}^n}{r_2} + \frac{\alpha_{23}^n}{r_3} + \frac{\alpha_{24}^n}{r_4}} \frac{k\prime[AgI]}{k\prime[AgI]} = \frac{\frac{0.2^n}{50} + \frac{0.3^n}{75} + \frac{0.4^n}{100} + \frac{0.1^n}{125}}{\frac{0.1^n}{50} + \frac{0.3^n}{75} + \frac{0.4^n}{100} + \frac{0.2^n}{125}} = 1.10$$

Analytically, this equation cannot be solved for *n*, but manual verification is rather simple. Order 0 is not possible, as in this case the rate would be the same in both experiments. Overall, this is a first order reaction, when we verify n=1, we obtain indeed 1.10 rate ratio. In this part, we don’t need to think about constant units or exact total surface area of the particles, as we only need relative data comparing the two experiments. Also, how tightly packed the particles are or the surface coverage do not affect the results.

22. Kinetics of oxygen diffusion

(a) We count 16 oxygen atoms which are all inside the cell, so there are 8 SiO_2 units. Alternatively, we can count that there are 8 silicon atoms in the cell: $8 \times 0.125 + 6 \times 0.5 + 4 \times 1 = 8$, and thus are 8 SiO_2 units.

(b) If in Si we take the main diagonal, we have a Si-Si bond on both ends of diagonal. Each bond is ¼ of the diagonal. When the Si is oxidised, the oxygen atom is placed between any two silicon atoms and Si-O-Si ensemble also continues to occupy ¼ of the diagonal, so the Si-O bond is $^1/_8$ of the main diagonal.

$$8d_{Si-O} = \sqrt{3}a \Rightarrow a = \frac{8}{\sqrt{3}} \cdot d_{Si-O} = \frac{8}{\sqrt{3}} \cdot 1.54 = 7.11A$$

The ratio between unit cells is 7.11 Å/5.43 Å = 1.31, so the volume ratio is $1.31^3 = 2.24$

(c) We have an equilibrium between O_2 molecules in the gas phase and in the bulk/soild (where O_2 is in an atomic state or we could say a SiO_2 state). Considering the Henry's law constant, the O_2 pressure in the chamber decreases as some of the oxygen enters into the bulk. From the other side, the thickness of the layer grows (we assumed that the surface area remains constant). In any case, the volume of the wafer is negligible compared to the volume of the chamber.

$$K = \frac{[O_2]}{p_{O2}} = \frac{\frac{n_{O_2}}{V_{Si}}}{p_0 - \frac{n_{O_2}RT}{V_{O_2}}} = \frac{\frac{n_{O_2}}{l \cdot S_{wafer}}}{p_0 - \frac{n_{O_2}RT}{V_{O_2}}} \Rightarrow \frac{n_{O_2}}{l \cdot S_{wafer}} = K \cdot \left(p_0 - \frac{n_{O_2}RT}{V_{O_2}} \right)$$

We have two unknown values, $n(O_2)$ and the thickness, l, but the thickness depends on $n(O_2)$.

When all the Si phase is transformed to SiO_2 ($n(O_2) = n(Si)$), the thickness of the layer will be 2.24 times larger (l=2.24×l_0) and $n(O_2) = n(Si) = 0.0167$ moles. When there is no O_2 (0.00 moles) we have (l=l_0).

So we could say that:

$$l = \left(1 + \frac{n_{O_2}}{0,01664} \cdot 1,24\right) \cdot l_0$$

$$\frac{n_{O_2}}{\left(1 + \frac{n_{O_2}}{0,01664} \cdot 1,24\right) \cdot V_{wafer}} = 2,35 \cdot \left(1,5 - \frac{n_{O_2} \cdot 0,082 \cdot 1200}{0,5}\right)$$

$$n_{O_2} = 2,35 \cdot (1,5 - 196,8 \cdot n_{O_2}) \cdot (1 + 13,88 \cdot n_{O_2}) \cdot 2 \cdot 10^{-4}$$

$$n_{O_2} = 6.7 \cdot 10^{-4} moles$$

$$l = \left(1 + \frac{6.7 \cdot 10^{-4}}{0.01664} \cdot 1,24\right) \cdot l_0 = 1.05 \cdot l_0 = 0.105cm$$

(d) If initially there was a 1 mm wafer, if the wafer became completely oxidised its thickness would increase up to 2.24 mm (as other two dimensions do not change). From part (c), the total wafer thickness is 1.05 mm at equilibrium, therefore the oxide thickness is:

$$x = 2.24 \cdot \frac{1.05 - 1}{2.24 - 1} = 0.09 mm$$

(e) If we consider a linearly decreasing oxygen concentration, the oxide layer will be twice as big as the previous value (i.e. 0.18 mm).

(f)

$$l_{0x}^2 + A \cdot l_{0x} = B(t+\tau) \text{ if } \tau = 0 \text{ we have } l_0^2 + Al_0 = Bt$$

We substitute the second equation in the first:

$$\left(l_{0x}^2 - l_0^2\right) + A\left(l_{0x} - l_0\right) = B$$

We obtain ***A*** = 473.2 nm, ***B*** = 94960 nm/h

(g) Alternatively, we could use a linear plot:

y=ax+b as $\left(l_{0x}^2 - l_0^2\right) = -A\left(l_{0x} - l_0\right) + B$

Where $y = l_{0x}^2 - l_0^2$ *and* $x = l_{0x} - l_0$ with -A value as the graph inclination and B the y value at x=0.

(h) Using the equation, we can solve the quadratic to determine l_{ox}.

$$(l_{ox}{}^2 - l^2) + A \cdot (l_{ox} - l) = B$$
$$(l_{ox}{}^2 - 2500^2) + A \cdot (l_{ox} - 2500) = B$$
$$(l_{ox}{}^2 - 2500^2) + 473.2 \cdot (l_{ox} - 2500) = 94960$$
$$l_{ox} = 2517.3 nm$$

(i) Thin Oxide Limit (Initial Growth Stage): When the oxide thickness is low the linear term dominates. The equation simplifies to:

$$l_{ox} \approx \frac{B(t+\tau)}{A}$$

This represents the linear growth regime.

Thick Oxide Limit (Long Time Growth): When the oxide thickness is high the quadratic term dominates. The equation simplifies to:

$$l_{ox}^2 \approx B(t+\tau)$$

This represents the parabolic growth regime.

(j) Starting at time zero, we have the initial growth stage which is linear

$$l_{ox} = \frac{B(t+\tau)}{A} \Rightarrow l_0 = \frac{B}{A} \cdot t \ \ when\ \tau = 0 \Rightarrow l_{ox} - l_0 = \frac{B}{A} \cdot \tau$$

t, min	0	5	8	12
t, h	0	1/12	2/15	1/5
l_{ox}	1000	1012.6	1019.9	1030.0
l_{ox}-l	0	12.6	19.9	30.0

We find ***B/A*** = 150, while for the previous experiment ***B/A*** = 200, so the temperature is not the same.

(k) B (boron): b) p.

P (phosphorus): a) n.

As (arsenic): a) n.

Ge (germanium): d) neither n nor p.

(l) For boron atoms: **c)**

For phosphorous atoms: **b)**

(m) The total thickness of the silicon and silicon dioxide layers are given as:

$$l_{Si} = 300\text{nm} = 300 \cdot 10^{-7}\text{cm} \quad and \quad l_{SiO_2} = 100\text{nm} = 100 \cdot 10^{-7}\text{cm}$$

Using the segregation coefficient, we have: $C_{Si} = K \cdot C_{SiO_2}$

The surface concentration of dopant is $10^{13} atoms/cm^2$

The total amount of dopant in both layers can be expressed as:

$$C_{Si} \cdot l_{Si} + C_{SiO2} \cdot l_{SiO2} = N_{total}$$

$$K \cdot C_{SiO2} \cdot l_{Si} + C_{SiO2} \cdot l_{SiO2} = N_{total}$$

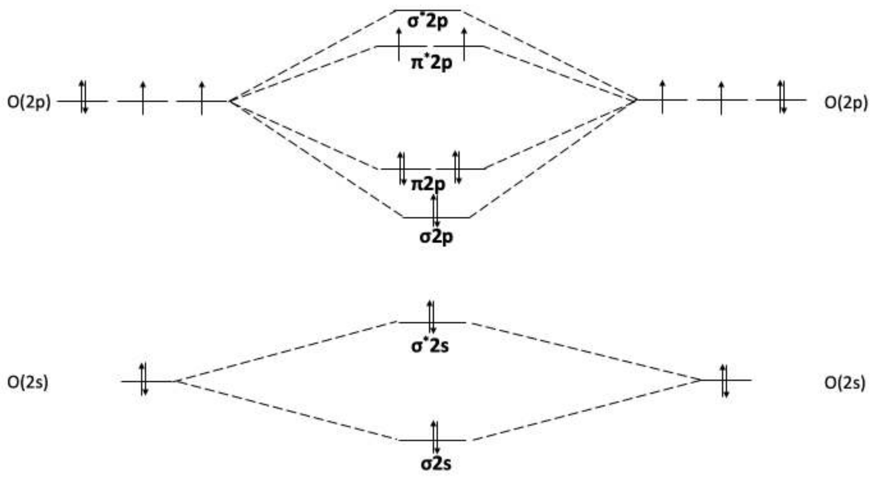
We obtain: $C_{SiO2} = \frac{N_{total}}{K \cdot l_{Si} + l_{SiO2}} = \frac{10^{13}}{0.7 \cdot 3 \cdot 10^5 + 1 \cdot 10^5}$

$$C_{SiO2} = 0.322 \cdot 10^{18}\ atoms \cdot cm^{-3}\ and\ C_{Si} = K \cdot C_{SiO2} = 0.7 \cdot 0.322 = 0.225 \cdot 10^{18}\ atoms \cdot cm^{-3}$$

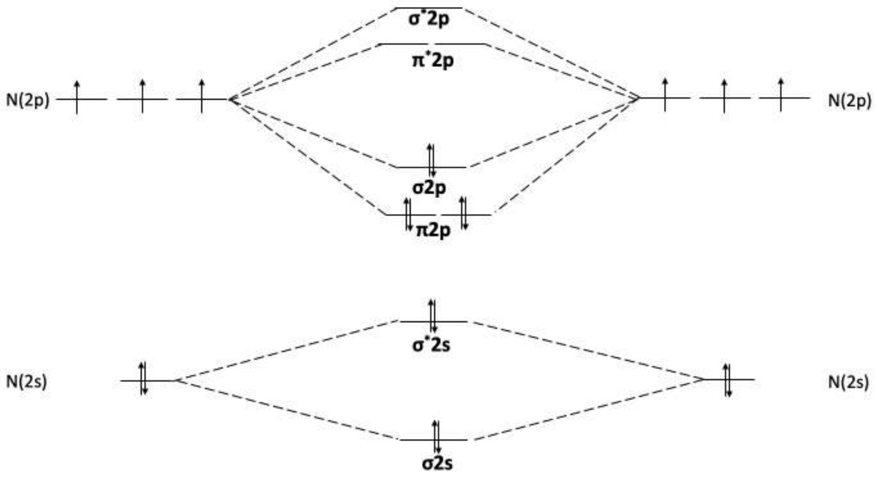
23. Molecular orbitals of diatomics

(a)

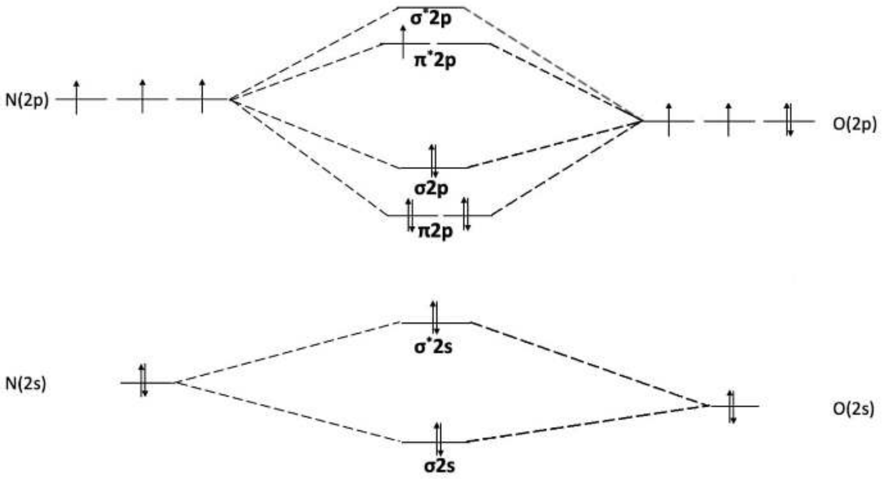
O_2 :



N_2 :



NO:



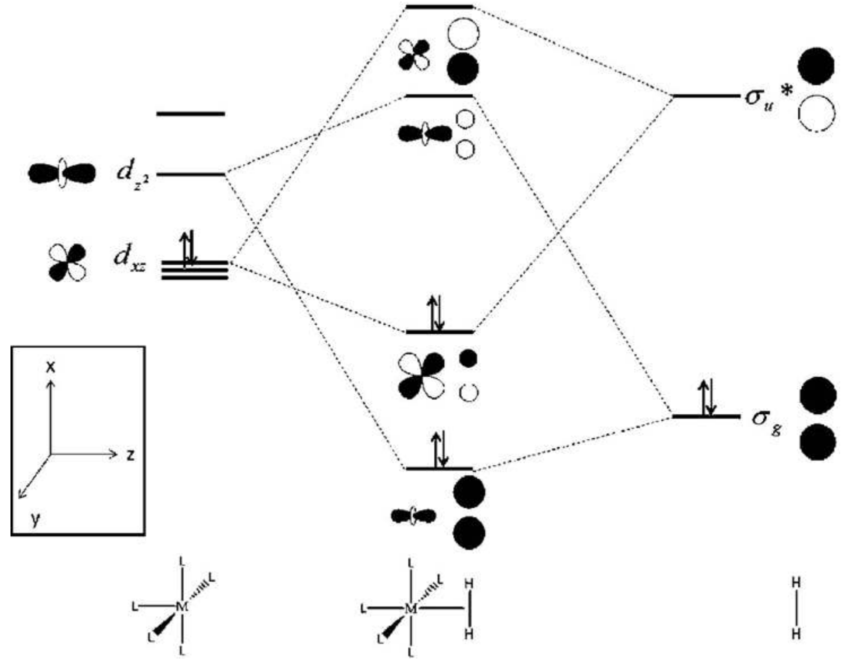
(b) In both NO and O_2 the electron is coming from an anti-bonding orbital. Therefore the highest ionisation energy belongs to N_2, as the electron is ionised from a bonding orbital. The relative position of NO and O_2 can be deduced from the fact that nitrogen atomic orbitals have a higher energy than those of oxygen. Therefore, the order is NO: 9.26 eV, O_2: 12.07 eV, N_2: 15.5 eV.

(c) Order of bond length (with bond orders given in brackets):
BaO_2 (1) > KO_2 (1.5) > O_2 (2) > $[O_2][PtF_6]$ (2.5)

(d) In H_2O_2 the O-O moiety has partial negative charge and resembles peroxide with a single bond. In O_2F_2 there is a partial positive charge which resembles the oxygen dication with a triple bond.

24. Coordination chemistry of dihydrogen

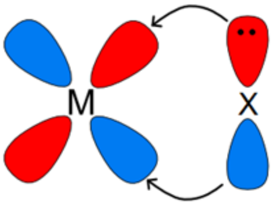
(a)



(b) $W(CO)_5(H_2)$ is dihydrogen complex while $Ir(PPh_3)_2(H)_2$ is a dihydrido complex. There are two reasons. Firstly, iridium(0) is a d^9 metal and therefore has more electron density occupying the anti-bonding σ* orbital of H_2, leading to more dihydrido character. The second reason is simply the coordination number. The tungsten complex would be six coordinate as dihydrogen and seven coordinate as dihydrido (which is high); the iridium complex would be three coordinate as dihydrogen (which is low) and four coordinate as dihydrido.

(c) $W(CO)_4(H_2)(PPh_3) > W(CO)_5(H_2) > W(CO)_4(H_2)Cl$. The transition from a dihydrogen character to a dihydrido character results from electrons occupying the the anti-bonding orbital of H_2. The more electron-rich the metal centre, the less dihydrogen character, and the longer the H-H distance. PPh_3 is less electron-withdrawing than CO, resulting in a more electron-rich metal. The chloride ligand has a formal negative charge, meaning that the chlorido complex is a d^5 system rather than d^6 and therefore less electron-rich.

(d)

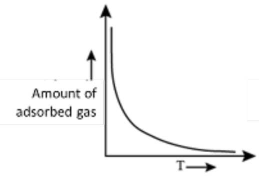


π donor ligand

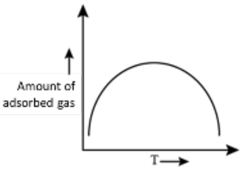
(e) $Ir(CO)_3I(H)_2$ > $Ir(CO)_3Cl(H)_2$ > $Ir(CO)_3F(H)_2$. The π-donating strength of halides increases with decreasing electronegativity, leading to a more electron-rich metal centre, which in turn gives the complex more dihydrido character and a higher bond length.

25. Adsorption and heterogeneous catalysis

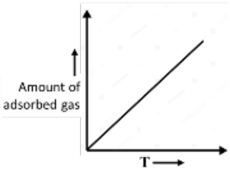
(a)



Physisorption



Chemisorption



(b) $T_1 < T_2 < T_3$

(c) (ii) ΔS is negative and ΔH should be highly negative.

(d) Al_2O_3, SiO_2.

(e) $0.05\ L\ N_2\ x\ \frac{1mol}{22.41\ L}\ x\ \frac{6.02x10^{23}\ molecule}{1mol}\ x\ \frac{0.16\ x\ 10^{-14}\ cm^2}{1\ molecule}\ x\ \frac{1m^2}{10^4\ cm^2} \times \frac{1}{0.5g} = 430\ \frac{m^2}{g}$

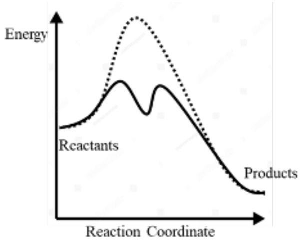
(f) (i) Nanoparticles provide higher surface areas.

(ii) Nanoparticles generally provide more active sites on the surface.

(iii) Nanoparticles allow the use of smaller amounts of expensive metal catalysts.

(g) $2CH_4 + O_2 \rightarrow 2CO + 4H_2$

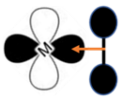
(h)



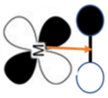
(i) Chemisorption. Since alkene hydrogenation involves H-H bond braking, the bond should be activated which can occur only through chemisorption.

(j) σ- and π-bonding

(k)



σ- bonding



π-bonding

26. Nitrogen chemistry

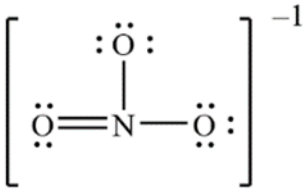
(a) From the mass percentage of iron in **D**, the molar mass of **D** can be calculated to be 227.66 g/mol, which is 65.46 g/mol higher than that of $FeCl_3$ and therefore the molar mass of gas **A**.

A: NOCl; **B**: NO_2; **C**: KNO_3; **D**: [NO][$FeCl_4$].

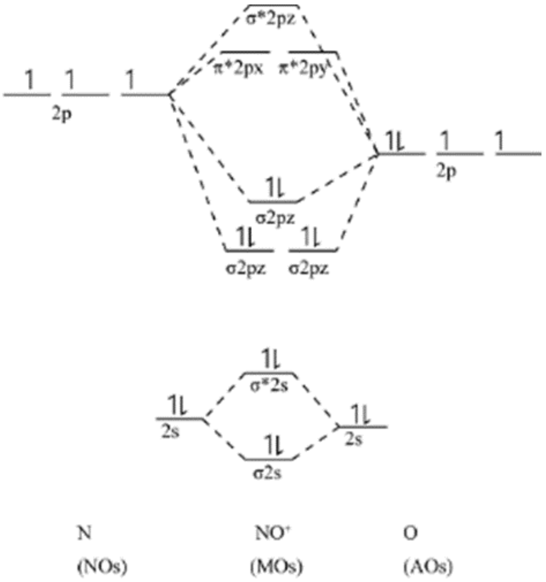
(b) **Reaction 1**: $KCl + N_2O_4 \rightarrow NOCl + KNO_3$

Reaction 2: $NOCl + FeCl_3 \rightarrow [NO][FeCl_4]$

(c)



(d)



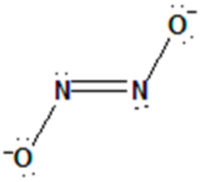
(e) 117 µL/min for 3 h × 1.44 g/mL = 30.326 g N_2O_4 = 0.33 mol. The loss in mass per mol is 65.46 g per mol = 21.6 g. Total mass of reactants is 30 g (KCl) + 30.326 g N_2O_4.

Therefore, final mass is 38.73 g.

(f) **E**: $C_5H_{11}ONO$; **F**: $Na_2[ON=NO]$; **G**: $Ag_2[ON=NO]$; **H**: AgCl; **I**: $H_2N_2O_2$

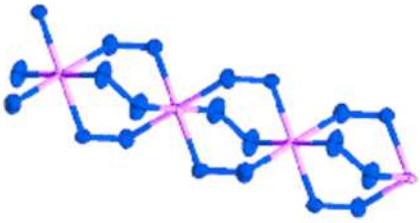
(g) $C_5H_{11}ONO + NH_2OH + 2NaOEt \rightarrow C_5H_{11}OEt + H_2O + EtOH + Na_2N_2O_2$

(h) The most stable form is the *trans* isomer.



(i) $[Co(N_2H_4)_3][ClO_4]_2$

(j)



(k) $[Co(N_2H_4)_3][ClO_4]_2 \rightarrow Co + 3N_2 + 6H_2O + Cl_2 + O_2$

(l) 58.69/353.746×100% = 16.6%

(m) For both cases it's the sum of all the gaseous products: 295.06 g/mol

(n) By comparing the mass loss at 1 min and 2 min we realise that the rate of mass loss is linear and constant:

	Rate (mmol/s)
Co (400 K)	0.10
Co (420 K)	0.12
Ni (400 K)	0.15
Ni (420 K)	0.17

E_a for Co: 12.7 kJ / mol   for Ni: 8.7 kJ / mol

(o) The only bonds that are present in the structure of these compounds are the M-N and N-N bonds. The answer cannot be the M-N bond since that bond is stronger for Ni but the nickel compound has a lower activation energy to decompose. Therefore the answer is B) N-N bond breaking.

27. Hot desert of unknown unknowns

(a) We can start with the **A-D** cycle. We know that **A** is a binary compound and most likely an oxide because it is formed in the decomposition of **D**. From the mass fraction we can calculate that **A** is CaO. From the scheme, we guess that **D** is $CaCO_3$ and **U** is CO_2. So, one of the elements (**X** or **Y**) is carbon.

From the structure of polymer **M**, we can understand that **X** has a valence of three (if all bonds are single) or four (if one of the bonds is double). Similarly, **Y** and **Z** could be bivalent or trivalent. So, **X** is carbon, because only it can be 4-valent. Then one of **Y** or **Z** is bivalent and the other is trivalent.

$CaO + 3C \rightarrow CaC_2 + CO$, so **B** is calcium carbide and **S** is CO. Without knowledge of the CaC_2 compound, it will be possible on the subsequent steps to understand that there are two carbon atoms. Compound **C** forms gas **T** and being binary **T** can contain only hydrogen as a second element. Looking through the gases where the central atom is divalent or trivalent, we do not find divalent options (e.g., H_2S is heavier than air). Of the trivalent options, NH_3 or B_2H_6 are possibilities. It is important to mention here that calcium carbide reacts with nitrogen to form calcium cyanamide $CaCN_2$, which upon reaction with water gives ammonia. This completes the cycle of reactions of **A-D**, and tells us that **Y** is nitrogen.

The conversion of **C**→**E** is not simple, but the main idea is that compound **E** must contain both carbon and nitrogen, and is most likely sodium cyanide, but this assumption can also be tested through identification of substance **F**. This provides further confirmation that **T** is NH_3.

Substance **F** has a molar mass of 34n g / mol according to the data on the mass fraction of oxygen:

$$M_F = \frac{16 \cdot n}{0.4705} = 34n\ g \cdot mol^{-1}$$

where n is the number of oxygen atoms and n is at least 2, since this substance also contains sodium. Assuming that the molecule has two oxygen atoms, its molecular weight is 68 g / mol. Subtracting two oxygen and one sodium, we get 13 g / mol, which corresponds to CH, so **F** is sodium formate, HCOONa.

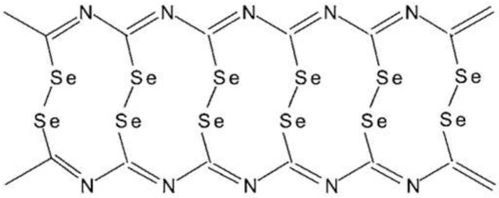
For the next step, we might assume that cyanide reacts with sulfur to form thiocyanate, but through calculations based on the data about **J** (2.02 g) and **K** (0.632 g), by subtraction we work out there is 1.388 g of **L**, and so we identify **Z** as selenium. For this we consider **J** as $(ZCN)_2$ and simple disproportionation to form compounds **K** and **L** as $Z(CN)_2$ and $Z_3(CN)_2$:

$$\frac{0.634}{1.386} = \frac{z + 26 \cdot 2}{3z + 26 \cdot 2} \Rightarrow z = 78$$

Now we have a complete list of all unknown compounds:

A CaO; **B** CaC_2; **C** $CaCN_2$; **D** $CaCO_3$; **E** NaCN; **F** HCOONa; **G** NaSeCN; **H** $Na[Ag(SeCN)_2]$; **I** AgSeCN; **J** $Se_2(CN)_2$; **K** $Se(CN)_2$; **L** $Se_3(CN)_2$; **S** CO; **T** NH_3; **U** CO_2;

M



(b)

$CaO+3C \rightarrow CaC_2 + CO$

$CaC_2 + N_2 \rightarrow CaCN_2 + C$

$CaCN_2 + 3HOH \rightarrow CaCO_3 + 2NH_3$

$CaCO_3 \rightarrow CaO + CO_2$

$CaCN_2 + Na_2CO_3 + C \rightarrow CaCO_3 + 2NaCN$

$NaCN + 2H_2O \rightarrow HCOONa + NH_3$

$NaCN + Se \rightarrow NaSeCN$

$NaSeCN + Ag^+ \rightarrow AgSeCN + Na^+$

$2NaSeCN + Ag^+ \rightarrow Na[Ag(SeCN)_2] + Na^+$

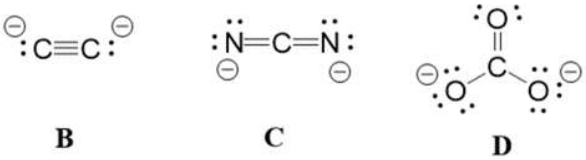
$Na[Ag(SeCN)_2] + Ag^+ \rightarrow 2AgSeCN + Na^+$

$2AgSeCN + I_2 \rightarrow (SeCN)_2 + 2AgI$

$2(SeCN)_2 \rightarrow Se(CN)_2 + Se_3(CN)_2$

$n(SeCN)_2 \rightarrow (NCSeSeCN)_n$

(c)



(d) The silver(I) cation is a soft acid, so it is more favourable for it to combine with a soft base (selenium containing anions) than with a hard base (carbon containing anions).

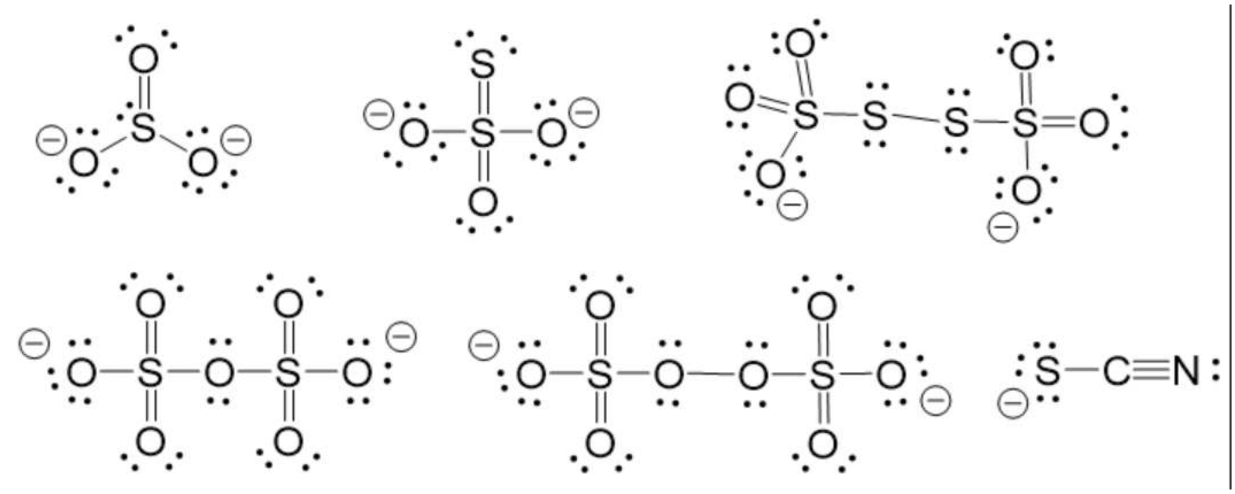
(e) Cyanamide

28. Analytical chemistry of the chalcogens

(a)

SO_3^{2-} (+4), $S_2O_3^{2-}$ (+2), $S_4O_6^{2-}$ (+2.5 as avarage or +5, 0, 0, +5), $S_2O_7^{2-}$ (+6), $S_2O_8^{2-}$ (+6), SCN^- (−2)

(b)



(c) The Henry's law constant could give the value of SO_2(aq) or $SO_2H_2O_{(aq)}$ which is the same.

$$\left[SO_3^{2-}\right]=\left[SO_{2(aq)}\right]\cdot\frac{K_1\cdot K_2}{\left[H^+\right]^2}\Rightarrow\left[H^+\right]=\sqrt{\frac{K_1\cdot K_2\cdot\left[SO_{2(aq)}\right]}{\left[SO_3^{2-}\right]}}=\sqrt{\frac{10^{-1.8}\cdot10^{-7.2}\cdot19.5\cdot10^{-9}}{10^{-6}}}=4.41\cdot10^{-6}\mathrm{M}$$

This concentration is not dependent on solution pH, but its molar fraction is dependent.

So pH should be greater than 5.36.

The solubility of SO_2 can be then calculated considering all S forms:

$$\left[S^T\right]=\left[SO_{2(aq)}\right]+\left[HSO_3^-\right]+\left[SO_3^{2-}\right]=\left[SO_{2(aq)}\right]\left(1+\frac{K_1}{\left[H^+\right]}+\frac{K_1\cdot K_2}{\left[H^+\right]^2}\right)$$

$$=19.5\cdot10^{-9}\cdot\left(1+\frac{10^{-1.8}}{10^{-5.36}}+\frac{10^{-1.8}\cdot10^{-7.2}}{\left(10^{-5.36}\right)^2}\right)=7.18\cdot10^{-5}M$$

(d) The quantity of the remaining forms should be 0.01% and it will be mostly the HSO_3^- form.

If we have a ratio $[SO_3^{2-}]/[HSO_3^-] = 10^4$ thus pH = pK_2 + 4.0 = 11.2

(e) The total solution volume is 200 mL and the initial concentrations of both solutions considering dilution are Na_2SO_3 (0.025 M) and $NaHSO_4$ (0.060 M).

First, an acid-base reaction occurs: $SO_3{}^{2-} + HSO_4{}^- \rightarrow HSO_3{}^- + SO_4{}^{2-}$

The pK of this reaction is 5.4, thus the equilibrium is completely shifted to the right giving 0.025 M of $HSO_3{}^-$ and $SO_4{}^{2-}$ and on the left only 0.035 M of $HSO_4{}^-$ remains.

Now we should consider the remaining equilibrium which will modify slightly calculated concentrations:

$$HSO_3{}^- + HSO_4{}^- \leftrightarrow SO_4{}^{2-} + H_2SO_3 \qquad pK = -pK_{a1}\left(H_2SO_3\right) + pK_{a2}\left(H_2SO_4\right) = 0.2$$

$$\frac{(0.025+x)x}{(0.025-x)(0.035-x)} = 10^{-0.2} \Rightarrow x = 0.008M$$

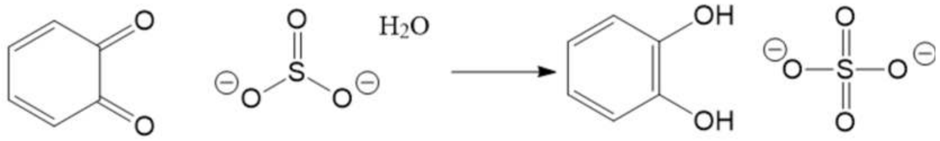
The solution pH we can calculate via the couple $HSO_4{}^-/\ SO_4{}^{2-}$ or via $H_2SO_3/\ HSO_3{}^-$

$$pH = pK_{a2}(H_2SO_4) + \log\frac{[SO_4{}^{2-}]}{[HSO_4{}^{2-}]} = 2.0 + \log\frac{0.033}{0.027} = 2.1$$

$$pH = pK_{a1}(H_2SO_3) + \log\frac{[HSO_3{}^-]}{[H_2SO_3]} = 1.8 + \log\frac{0.017}{0.008} = 2.1$$

(f) If we write both half-reactions, we will see H^+ on the left side of the reduction process. So when pH is increasing we have less H^+ and so the equilibrium moves to the left, so the potential decreases (=redox potential is decreasing).

(g) From the standard potentials, we could find the equilibrium constant for the redox reaction:



which is $K = exp\left(\frac{n\Delta E^0 F}{RT}\right) = exp\left(\frac{2\cdot(0.69-0.24)\cdot 96500}{8.31\cdot 298}\right) = 1.7\cdot 10^{15}$

In the first case (c = 0.099 M), the total reduction is not possible, as the sulfite concentration is less than the quinone concentration, so even without equilibrium calculations we can say that at least 0.001 M of quinone will remain.

For the second case (c = 0.100 M), both initial concentrations are the same thus:

$$K = \frac{[H_2Q][SO_4{}^{2-}]}{[Q][SO_3{}^{2-}]} = \frac{(0.1-x)^2}{x^2} = 1.7\cdot10^{15} \Rightarrow x = \left[Q\right] = 2.42\cdot10^{-9}M$$

thus the concentration is slightly bigger than the limit value. So, it is incomplete.

For the last case it is tricky to make the equation, so the easiest way is to consider that we need the concentration of quinone to be 10^{-9} M and estimate the necessary reaction quotient K' for it:

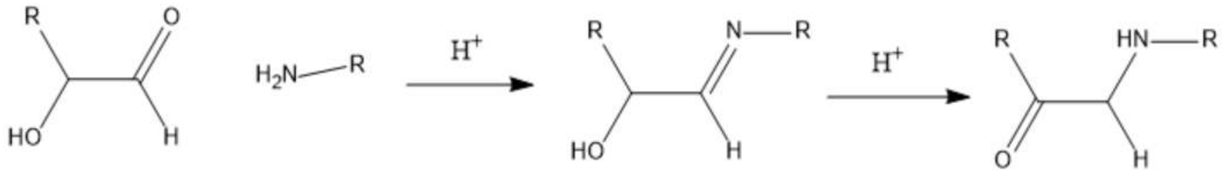
$$K\prime = \frac{[H_2Q][SO_4{}^{2-}]}{[Q][SO_3{}^{2-}]} = \frac{0.1\cdot0.1}{10^{-9}\cdot10^{-3}} = 10^{10} < K$$

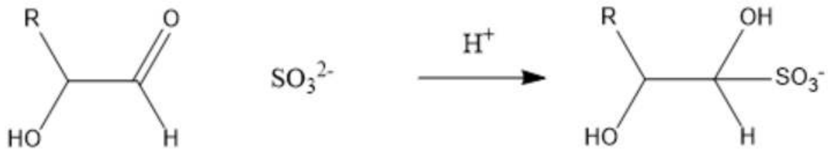
Therefore, to reach the *K* value, the numerator should increase and the denominator decrease, which chemically means that the quinone concentration becomes smaller and so the reaction is complete.

NB: For those who calculate the exact value of the quinone concentration you will find a value of $5.9\cdot10^{-15}$ M, and then you could notice that the quinone concentration in the second case is the geometric average of the first and the third cases.

(h) There is no dependence on pH.

(i)





(j)

$RNH_2 + H^+ \rightarrow RNH_3^+$ decreasing the nucleophilicity, so pH should not be too low.

$RCH(OH)CHO + H^+ \rightarrow RCH(OH)CHOH^+$ this reaction increases the electrophilicity of the carbon atom, so pH of the solution should not be too high.

$SO_3^{2-} + 2H^+ \rightarrow SO_{2(g)} + H_2O$ sulfite ion leaves in form of SO_2 gas, so pH should not be too low.

$SO_3^{2-} + 2HNO_3 \rightarrow SO_4^{2-} + 2NO_2 + H_2O$, so acid cannot be good a oxidant (or good a reductant).

(k)

$$\mathrm{SO_3^{2-} + 2H^+ \rightarrow SO_2 + H_2O}$$

$$\mathrm{SO_2 + H_2O_2 \rightarrow SO_4^{2-} + 2H^+}$$

$$\mathrm{H_2\,SO_4 + NaOH \rightarrow NaHSO_4 + H_2O} \quad \text{or} \quad \mathrm{H_2\,SO_4 + 2NaOH \rightarrow Na_2\,SO_4 + 2H_2O}$$

$$\mathrm{SO_3^{2-} + I_2 + H_2O \rightarrow SO_4^{2-} + 2\,HI}$$

(l) As selenate ion is more oxidising than a sulfate ion, so we can only state that a sulfate ion will not be reduced by a chloride ion, but we cannot conclude about bromide and iodide ions from these data.

(m) $2\ Au + 3\ H_2SeO_4 \rightarrow Au_2(SeO_3)_3 + 3\ H_2O$

(n) **A**: $Au_2(SeO_3)_2(SeO_4)$

$2\ Au + 4\ H_2SeO_4 \rightarrow Au_2(SeO_3)_2(SeO_4) + H_2SeO_3 + 3H_2O$

B: $Au_2(SeO_3)_2O$

$2\ Au + 3\ H_2SeO_4 \rightarrow Au_2(SeO_3)_2O + H_2SeO_3 + 2H_2O$

29. Vibrational modes

(a) The number of normal modes of a linear molecule with N atoms can be calculated as 3N−5. There are four normal modes for CO_2: symmetric stretching, asymmetric stretching, and two bending modes.

(b) Only two bands are expected to be found in the IR spectrum of CO_2.

- the symmetric stretching (1340 cm^{-1}) is infrared inactive.
- the asymmetric stretching shows at 2350 cm^{-1}.
- the bending modes are doubly degenerate (same energy), giving rise to only one band at 667 cm^{-1}.

(c) The number of normal modes of a non-linear molecule with N atoms can be calculated as 3N−6. There are three normal modes for SO_2: symmetric stretching, asymmetric stretching, and bending.

(d) The frequency of the vibration can be calculated as: $\nu = \overline{\nu} \cdot c$

For the S=O bond $\nu = 3.45 \times 10^{13}\ s^{-1}$

$m_S = 5.32 \times 10^{-23}$ g and $m_O = 2.66 \times 10^{-23}$ g

$k = 8.33 \times 10^5\ dyn{\cdot}cm^{-1} \cong 833\ N{\cdot}m^{-1}$

(e) The energy can be estimated as $E_{osc} = h\nu = 2.29 \times 10^{-20}$ J.

(f) For the same pair of elements, a single bond has a lower force constant than a double bond; the frequency of the stretching vibrations is lower. In the IR spectrum, the stretching bands are shifted to lower wavenumbers.

(g) The water molecule has three normal modes which results in bands at ~3756, 3657, and 1595 cm^{-1} (for free water molecules). In the solid matrix these values are slightly shifted, but can be distinguished from the sulphate anion bands, which appear in the range of approx. 1100-1200 cm^{-1} and around 650 cm^{-1}. The spectrum of anhydrite is c).

30. Applications of infrared spectroscopy to coordination chemistry

Part A

(a) Free NO_2^- would show three bands in the IR spectrum (symmetric stretching, asymmetric stretching, and bending). Upon coordination through the nitrogen atom, vibrations of M-NO_2 resemble those of a tetrahedral molecule, including a M-N stretching band at lower frequencies, and the rocking and wagging modes. When the coordination occurs through one oxygen atom, the N-O bonds are no longer equivalent, and each one has its own stretching frequency. This results in the appearance of an additional band in the nitrito spectrum, at 1065 cm^{-1} and the disappearance of the band at 823 cm^{-1}. Additionally, the stretching of the N-O double bond shifts to 1452 cm^{-1}.

(b) Spectrum a) nitrito isomer

Spectrum b) $[Co(NH_3)_5Cl]Cl_2$

Spectrum c) nitro isomer

Part B

(c) As a diatomic molecule, CO has only one vibrational mode, a stretching mode, which has a wavenumber close to 2140 cm^{-1}.

Complexes of general formula $[M(CO)_6]^{x+}$ have a total number of 33 vibrational modes, but only four of them are IR active (originating from a change in the dipole moment of the molecule during the vibration). These are the C-O and M-C stretching modes, and the M-C-O and C-M-C bending modes. The latter appear at wavenumbers that are lower than measured by routine laboratory FTIR spectrometers (less than 100 cm^{-1}).

(d) There are two possible geometric isomers: *cis* and *trans*.

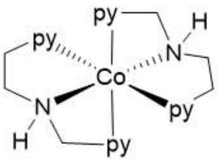
(e) Around 2100 cm^{-1} the coordinated C-O bond stretching bands can be found. Depending on the relative position of ligands L and CO, there is going be a modification in the dipole moment of the molecule with each vibration. The higher symmetry in the trans *isomer* implies that a lower number of bands would be IR active.

Part C

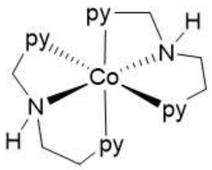
(f) Both pepma and bpma are tridentate ligands. Considering the L/Co^{2+} molar ratio and the fact that both **A** and **B** are mononuclear compounds, the complex species $[CoL_2]^{2+}$ should be formed. The presence of a strong band at ~1100 cm^{-1} in the IR spectra indicates that perchlorate is present in the molecular formula of both products, as a counterion.

A = $[Co(pepma)_2](ClO_4)_2$ and **B** = $[Co(bpma)_2](ClO_4)_2$

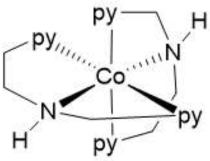
The possible isomers for $[Co(pepma)_2]^{2+}$ are:



fac isomer (1)



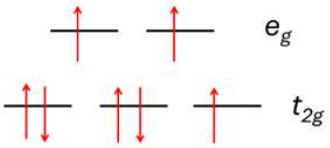
fac isomer (2)



mer isomer

The *fac* isomer (1), where the equivalent groups are *trans* to each other is the one experimentally obtained.

(g) The experimental magnetic moment corresponds to a high-spin Co^{2+} ion in an octahedral field:



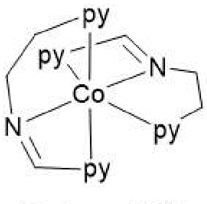
The electron configuration is: $t_{2g}^5\ e_g^2$.

(h)

1100 cm^{-1}: Cl=O stretching from perchlorate

3292 and 3185 cm^{-1}: N-H stretching from the secondary amines

(i) In the reaction of **A** with oxygen, the metal ion remains in the same oxidation state (same magnetic moment), meaning that the oxidation occurs on the ligand. This results in a new band in the IR spectrum, which is due to the formation of a C=N double bond, since the secondary amine reacts to form an imine, as follows:



$[Co(pepmi)_2]^{2+}$

The elemental analysis of **A** and **C** are similar because their mass only differs by four hydrogen atoms.

Compound **D** is diamagnetic, which means that Co^{2+} was oxidised to Co^{3+}. Octahedral Co^{3+} complexes are typically low spin t_{2g}^6 systems. This also means there must be three perchlorate anions in **D**, which is in agreement with **B** and **D** having different elemental analysis. The formula of **D** is $[Co(bpma)_2](ClO_4)_3$.

IChO 2025

Solutions

Practical Prep Problems

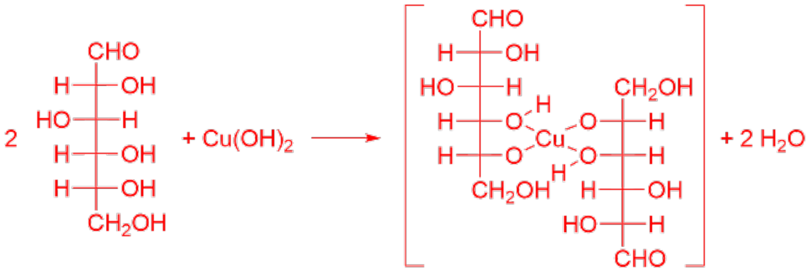
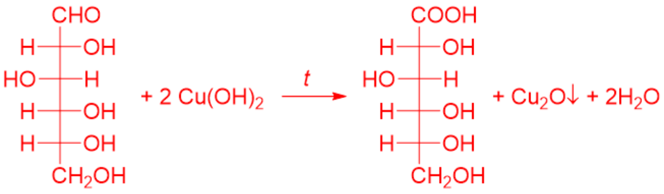
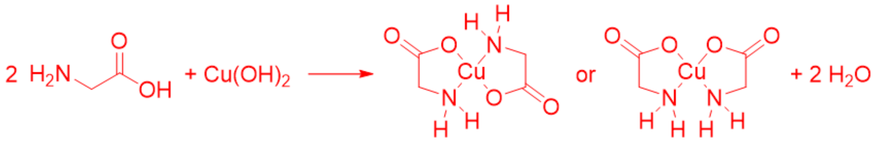
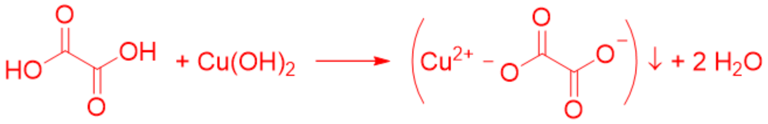
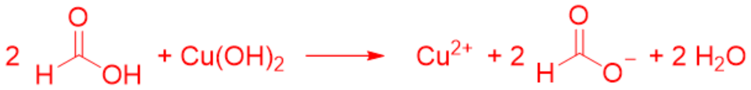
P1. Qualitative analysis of organic compounds

PART A:

1)

Vial	**A1**	**A2**	**A3**	**A4**	**A5**
Observations	Blue precipitate dissolves forming dark blue solution. When heated, red precipitate is formed.	Blue precipitate dissolves forming dark blue solution. No changes when heated.	Blue precipitate first dissolves and then light blue precipitate is formed.	Blue precipitate dissolves forming light blue solution.	No changes, blue precipitate turns black when heated.
Compound	Glucose	Glycine	Oxalic acid	Formic acid	Acetone

2)

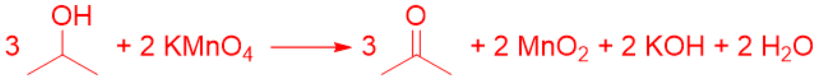
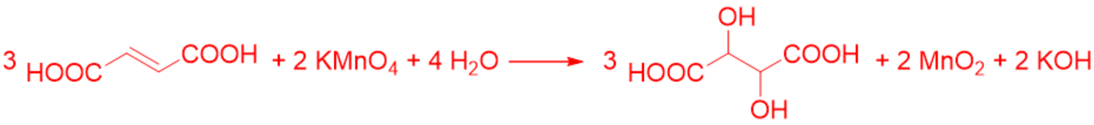
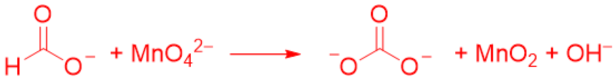
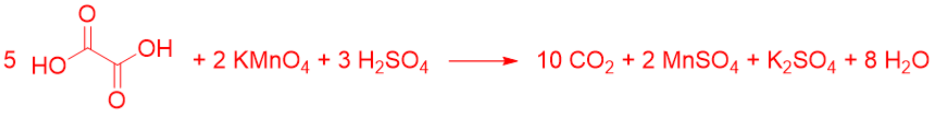
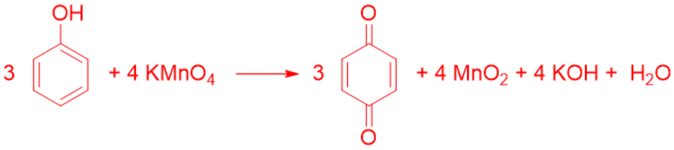
Compound	Reaction(s)
Glucose	 (any other reasonable structure of the complex is accepted)  (the reaction can be written starting from the complex but in that case, not all coordinated glucose molecules will be oxidised)
Glycine	
Oxalic acid	
Formic acid	
Acetone	$Cu(OH)_2 \longrightarrow CuO\downarrow + H_2O$ (no reaction with acetone)

PART B:

1)

Vial	**B1**	**B2**	**B3**	**B4**	**B5**
Observations	Purple solution turns red and then slowly brown. When heated, brown solution is formed.	Immediate discolouration when $KMnO_4$ is added dropwise. When more $KMnO_4$ is added, the solution turns yellow.	Purple solution immediately turns green, which then slowly turns brown.	Purple solution slowly turns yellow, which slowly fades. Upon further addition of $KMnO_4$ the reaction proceeds faster (autocatalysis).	Dark brown precipitate is formed.
Compound	Propan-2-ol	Maleic acid	Sodium formate (+ NaOH)	Oxalic acid (+ H_2SO_4)	Phenol

2)

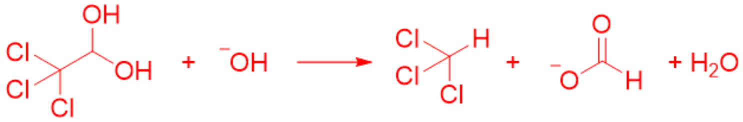
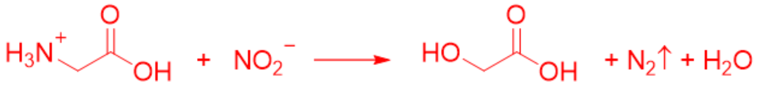
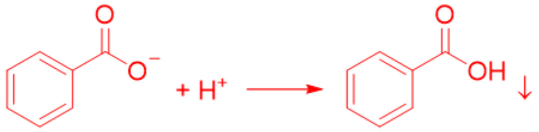
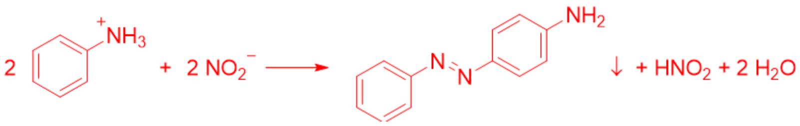
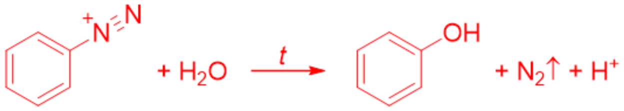
Compound	**Reaction(s)**
Propan-2-ol	 (one of the possible reactions)
Maleic acid	 (oxidation can proceed further)
Sodium formate (+NaOH)	 Further reduction of manganate is observed as green solution turns brown: 
Oxalic acid (+H_2SO_4)	
Phenol	 (the real product formed is 1:1 complex of hydroquinone and benzoquinone, called quinhydrone)

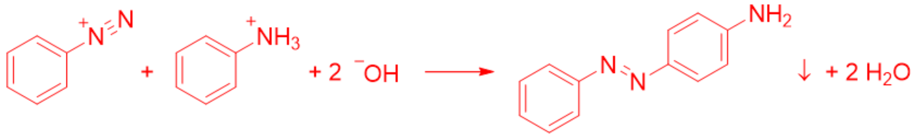
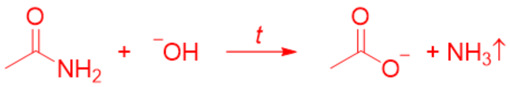
PART C:

1)

Vial	**C1**	**C2**	**C3**	**C4**	**C5**
Observations with H_2SO_4	–	–	White precipitate is formed.	–	–
Observations with NaOH	Turbid solution, which slowly gets separated into two phases.	–	–	–	No visual changes. When heated, a distinct smell of ammonia appears.
Observations with $NaNO_2$	–	Active fizzing, no colour change.	–	Yellow precipitate is formed. If acidified first with H_2SO_4 and then $NaNO_2$ is added, yellow solution is formed, which produces bubbles when heated and forms yellow precipitate when more of **C4** and then some NaOH are added.	–
Compound	Chloral hydrate	Glycine hydrochloride	Sodium benzoate	Aniline hydrochloride	Acetamide

2)

Compound	Reaction(s)
Chloral hydrate	
Glycine hydrochloride	
Sodium benzoate	
Aniline hydrochloride	If $NaNO_2$ is added directly to the aniline hydrochloride solution, a direct formation of the azo dye (Aniline Yellow) is observed:  If first H_2SO_4 was added before adding $NaNO_2$, then the formation of diazonium salt is observed:  When heated, the diazonium salt decomposes and fizzing is observed:  The addition of extra aniline hydrochloride to the diazonium salt solution, followed by the addition of some NaOH leads to the formation of the azo dye (Aniline Yellow):

	 Note: The reaction between PhN_2^+ and $PhNH_2$ can also produce triazene Ph-N=N-NH-Ph, which should be accepted as the correct answer as well. The preference for either azo dye or triazene depends on the reaction conditions, which is not expected to be known by the participants.
Acetamide	

P2. Sørensen formol titration

1) $H^+ + OH^- \rightarrow H_2O$

$$c(\mathrm{NaOH}) = \frac{c(\mathrm{NH_4^+}) \cdot V(\mathrm{NH_4^+})}{V(\mathrm{NaOH})} = \frac{0.1000 \cdot 5.00}{V_1}$$

The concentration of NaOH used during testing was 0.1000 M.

2) The expression to find the total amount of amino acids:

$$n(\mathrm{AA}) = \frac{100.0 \cdot c(\mathrm{NaOH}) \cdot V_2}{10.00 \cdot 1000}$$

3) The system of equations:

$$n(\mathrm{AA}) = n(\mathrm{AA_1}) + n(\mathrm{AA_2})$$
$$m(\mathrm{AA}) = M(\mathrm{AA_1}) \cdot n(\mathrm{AA_1}) + M(\mathrm{AA_2}) \cdot n(\mathrm{AA_2})$$

By solving this system of equations, one finds the amount of each amino acid and can now find the mass fractions:

$$\omega(\mathrm{AA_1}) = \frac{M(\mathrm{AA_1}) \cdot n(\mathrm{AA_1})}{m(\mathrm{AA})} \cdot 100\%$$
$$\omega(\mathrm{AA_2}) = \frac{M(\mathrm{AA_2}) \cdot n(\mathrm{AA_2})}{m(\mathrm{AA})} \cdot 100\%$$

P3. Determination of cysteine oxidation degree by two-phase titration

Step 1:

1) Appearance of red colour: $Fe^{3+} + SCN^{-} = FeSCN^{2+}_{(aq)}$ (red)

2) The expression to find the concentration of $AgNO_3$ according to the Volhard titration:

$$c(\mathrm{AgNO_3})_1 = \frac{c(\mathrm{KSCN}) \cdot V(\mathrm{KSCN})}{V(\mathrm{AgNO_3})} = \frac{0.1000 \cdot V_1}{5.00}$$

3) Change of colour from faint green to faint pink.

Dichlorofluorescein is an adsorption indicator. Before the equivalence point, there is an excess of Cl^{-} ions, which are adsorbed on the surface of AgCl particles, making them negatively charged. Dichlorofluorescein is only attracted to positively charged particles, therefore, the green colour of the free indicator is observed. After the equivalence point, there is an excess of Ag^{+} ions, which due to adsorption on AgCl particles, make them positively charged. These particles attract dichlorofluorescein, which due to adsorption changes colour to pink.

4) The expressions to find the concentration of $AgNO_3$ according to the Fajans titration and the average concentration based on two methods:

$$c(\mathrm{AgNO_3})_2 = \frac{c(\mathrm{NaCl}) \cdot V(\mathrm{NaCl})}{V(\mathrm{AgNO_3})} = \frac{0.1000 \cdot 5.00}{V_2}$$

$$c(\mathrm{AgNO_3}) = \frac{c_1 + c_2}{2}$$

The concentration of $AgNO_3$ used during testing was 0.1000 M.

5) Without dextrin, better coagulation of precipitate is observed, and the transition becomes less sharp. Dextrin, therefore, functions as an anticoagulant. When it is used, AgCl particles are well dispersed ensuring more efficient adsorption of indicator after the equivalence point.

Step 2:

Possible dilution procedure: 10.00 cm^3 in 100 cm^3, then 5.00 cm^3 in 100 cm^3.

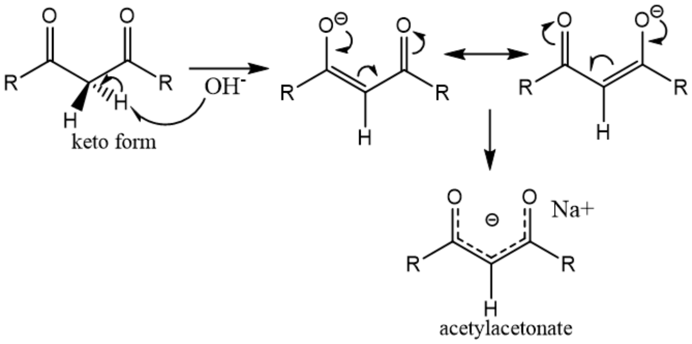
6) The expression to find the cysteine oxidation degree:

$$\text{Oxidation degree, \%} = \left(1 - \frac{c(\text{Cys})}{c(\text{Cys})_0}\right) \cdot 100\% = \left(1 - \frac{c(\text{AgNO}_3) \cdot V_3}{V(\text{Cys}) \cdot c(\text{Cys})_0}\right) \cdot 100\%$$

$$= \left(1 - \frac{c(\text{AgNO}_3) \cdot V_3}{10.00 \cdot 4.0 \cdot 10^{-4}}\right) \cdot 100\%$$

P4. Synthesis and characterisation of a paramagnetic cobalt acetylacetonate complex

1.1) Mechanism of the deprotonation of β-diketone with NaOH.



1.2) Magnetic Susceptibility of the complex 'A' has been measured using a Gouy balance and the data is given in the below table (Table 1):

Compound	L(mm) Sample	weight (g) Sample	Volume Susceptibility (χ_v)	Gram Susceptibility (χ_v)	Molar mass (g/mol)	T(K)
$Co_1O_6C_{10}H_{18}$	21.00	0.0879	0.106×10^{-4}	0.346×10^{-4}	293.2	298

1.3)

a) Molar susceptibility of this complex X_m:

Molar mass of complex A = 293.18 g/mol

Gram susceptibility obtained from the Gouy balance: 0.346×10^{-4} cc/g

Molar susceptibility $(\chi_M) = \chi_g \times$ molar mass

$= 0.346\times10^{-4}$ cc/g × 293.18 g/mol

$= 0.010144$ cc/mol

b) Spin only Effective magnetic moment (μ_{eff}) in BM (Bohr's magnetons) of the complex can be determined using the following formula.

$$\mu_{eff} = 2.828\sqrt{\chi_M \times T}$$

$$\mu_{eff} = 2.828\sqrt{0.010144 \times 298} \qquad \mu_{eff} = \underline{\underline{4.91\ \mathrm{BM}}}$$

c) Number of unpaired electrons

Number of unpaired electrons in compound A: 3

$\mu_{eff(\text{spin only})} = \sqrt{n(n+2)}$ here n = number of unpaired electrons

The observed μ_{eff} value (4.91 BM) corresponds to 3 unpaired electrons at the metal center

Oxidation State of the Co center is therefore: +2

Note: the effective magnetic moment observed for the compound A (4.91 BM) is greater than the magnetic moment calculated from the spin only formula. This indicates that in addition to the spin angular momentum, the moment arising from the orbital motion of the electrons also contributes to the observed magnetic moment. For first row transition metals ions, the orbital contribution to the magnetic moment usually arises from a partially filled t_2g *(*d_{xy}, d_{yz}, d_{xz}*) orbital configuration.*

2.2) Using a Gouy or faraday balance, record the magnetic susceptibility of the complex B

Magnetic Susceptibility of the compound 'B' has been investigated using a Gouy balance

Complex B behaves like a diamagnetic material

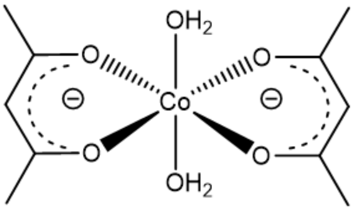
Volume magnetic susceptibility X_v observed is zero

3.1) Concenration of the Cobalt in Solution A can be determined using the Beer-Lambert Law: $A = \varepsilon cl$

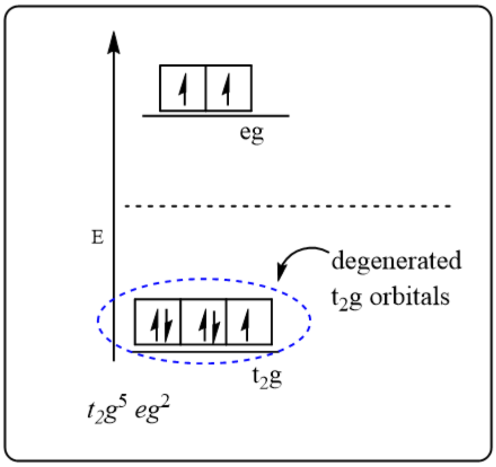
Concentration $c = A/\varepsilon l$ here $\varepsilon = 1.45x10^{4}\ cm^{-1}.l\ .mole^{-1}$, l = 1 cm A= absorbance measured at 500 nm

3.2) Using the magnetic data, provide the following information for the complex A

- Ground Spin state: 3/2 (high spin)
- Oxidation state of the Co center: Co^{+2}
- Most probable geometry: Octahedral geometry
- Draw the structure of the complex



- Draw the possible d orbital splitting for this complex with electronic distribution

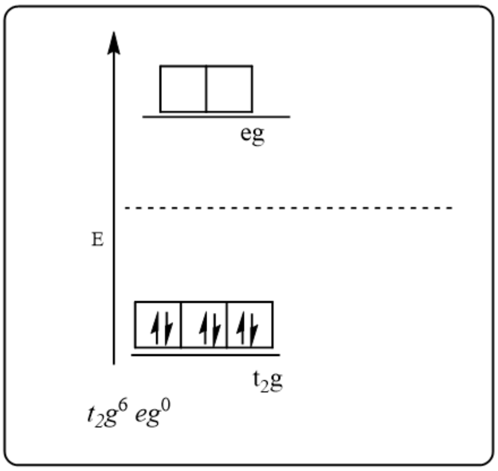


Co^{+2} high spin state

3.3) Using the magnetic data, provide the following information for the complex B

- Ground Spin state: zero

- Oxidation state of the 'Co' center: Co^{+3}
- Most probable geometry: Octahedral geometry
- Draw the possible d orbital splitting for this complex with electronic distribution



Co^{+3} low spin state

3.4) From your observation, how does the oxidation at the metal center affect the magnetic behavior and spin state of the complex A?

Oxidation at the cobalt center drastically changes the magnetic behavior.

Compound A with Co^{+2} is paramagnetic with a high spin electronic configuration.

Compound B with Co^{+3} is diamagnetic with a low spin electronic configuration.

P5. Never late with thiosulfate

(a)

1. $H_2O_2 + 2\ KI \rightarrow 2\ KOH + I_2 + H_2O$
2. $I_2 + 2\ Na_2S_2O_3 \rightarrow 2\ NaI + Na_2S_4O_6$

(b) As we see from the reaction, the neutralisation of the base OH^- by H^+ will shift the equilibrium toward the products with increasing H^+ concentration.

(c) Dextran, Amylose

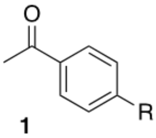
(d) The linear dependence should be observed - so the order is 1.

(e) The second clock will not have the instant colour change because the solution is not homogeneous, we should to continue to work with tubes.

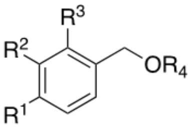
(f) The colour should change in two "chemical minutes" showing that decrease in concentration two times leads to a decrease in reaction rate of two times, therefore 1st order kinetics.

(g) In this case the solution of H_2O_2 which has been 2 or 3 times diluted, it should show 4 or 6 "chemical minutes".

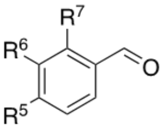
P6. To condense or not to condense?



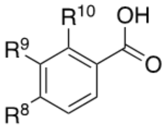
1



2



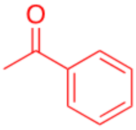
3



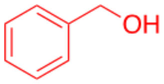
4

For the test of the task the following red chemicals were used. The chemicals 2 and 3 were dissolved in EtOH (3 mL) and the solutions were tested.

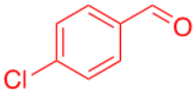
If any substitution of the chemicals is made, it is recommended to test the alternatives (for instance, *p*-anisaldehyde can be used instead of *p*-Cl-benzaldenyde). After the appropriate chemicals are chosen, it is recommended to insert appropriate GHS codes of the chemicals in the table at the end of the test paper.



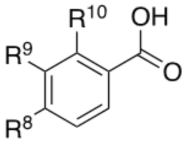
1



2A



3B



4

Part A: Condensation reaction with compounds A and B

Reaction between **1** and **3B**.

Q1: Choose the appropriate answer about the observations below (reaction mixture 1+2A).

Is it possible to distinguish reaction completeness by this TLC?	Yes/No
Is it better to use another eluent mixture?	Yes/No
Is reaction completed?	Yes/No/Unknown
Is there a product formation observed by TLC?	Yes/No/Unknown
Is there any visible sign of the reaction (gas evolution or precipitate formation)?	Yes/No

Q2: Choose the appropriate answer about the observations below (reaction mixture 1+3B).

Is it possible to distinguish reaction completeness by this TLC?	Yes/[✓ No]
Is it better to use another eluent mixture?	[✓ Yes]/No
Is reaction completed?	Yes/No/[✓ Unknown]
Is there a product formation observed by TLC?	Yes/No/[✓ Unknown]
Is there any visible sign of the reaction (gas evolution or precipitate formation)?	[✓ Yes]/No (Precipitate was formed in the reaction)

Reaction mixture A after H_2O added	Reaction mixture B after H_2O added
	

Q3: According to the observations, choose the correct structures for compounds **A** and **B** in the table below.

2: A	3: B	4: -

Q4: Which property/properties of compounds 2-4 allowed you to differentiate between them? Choose all that applies.

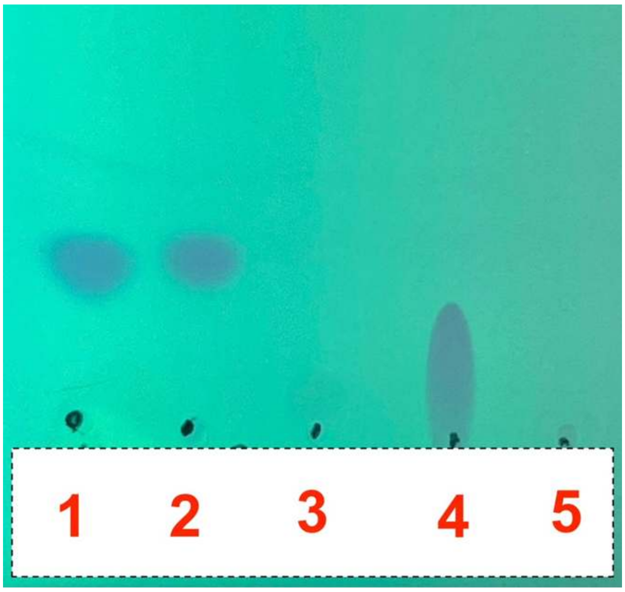
A. Magnetic properties.

B. Red-Ox properties.

C. Acid-base properties.

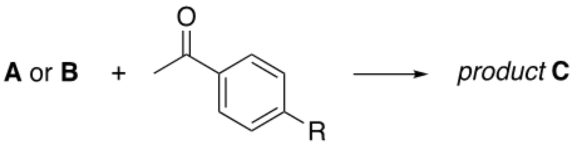
D. Electrochemical properties.

E. Photophysical properties. (compound 2A poorly absorbs UV-light)

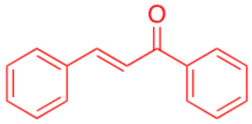


On the picture above, TLC of compounds **1-4** is presented. Additionally, lane 5 demonstrates TLC of compound **4** ($PhCO_2H$) in the same reaction mixture described in the task but with compound **4** (sodium salt of acid is formed which is poorly soluble in EtOAc, thus, almost invisible spot stays at the starting line).

Part B: product analysis



Q5: Answer the questions below and draw the structure of product C. Assume that all the substituents (R and Rn) are hydrogens for the product structure.

Was there a gas evolution?	Yes/[✓ No]
Was there a precipitate formation?	[✓ Yes]/No
Was there a colour change?	[✓ Yes]/No
Is it possible to detect this chemical on TLC by permanganate stain visualization instead of UV visualization?	[✓ Yes]/No
Structure of C	

Part C: more condensations?

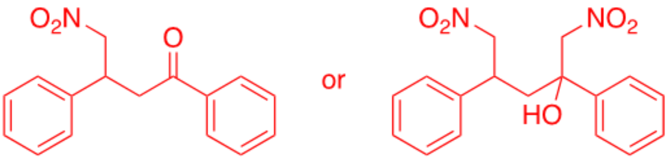
1 - reaction mixture concentrated

2 - reaction mixture diluted

3 - product C

Nitromethane is invisible on TLC plate undet UV visualization.

Q6: Draw a possible structure of product D that can be formed in the reaction performed. Assume that all the substituents (R and R^n) are hydrogens for the product structure.



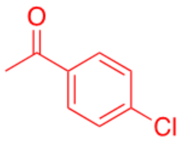
Q7: Choose the appropriate answer about the observations below.

Is it possible to distinguish reaction completeness by this TLC?	[✓ Yes]/No
Is it better to use another eluent mixture?	Yes/[✓ No]
Is reaction completed?	Yes/[✓ No]/Unknown
Is there a product **D** formation observed by TLC?	[✓ Yes]/No/Unknown

Part D: what are the products?

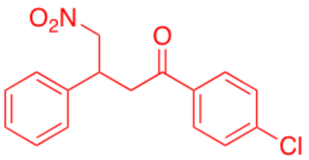
Q8: Draw the structures of compounds 1 and D that fit the presented spectra.

1



Chemical Formula: C_8H_7ClO
Molecular Weight: 154.5930

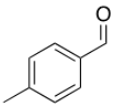
D

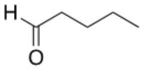


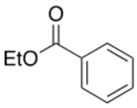
Chemical Formula: $C_{16}H_{14}ClNO_3$
Molecular Weight: 303.7420

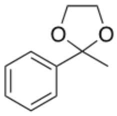
P7. Breakfast of carbonyls

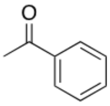
The list of chemicals tested:

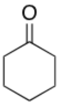

1
B-1

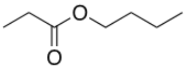

3
E-3


5
C-5

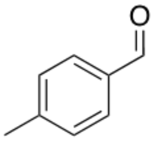
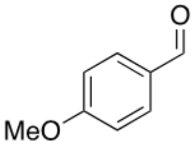
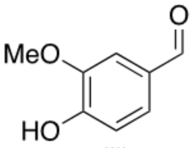
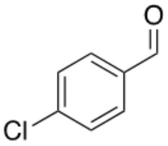
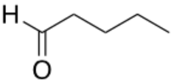
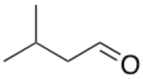
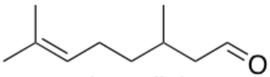
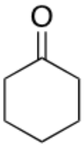
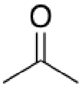
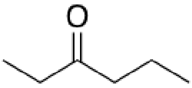
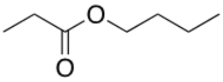
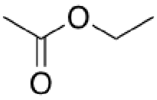
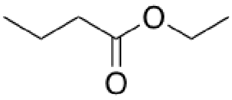

7
G-7


2
A-2


4
D-4


6
F-6

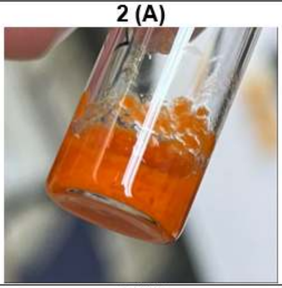
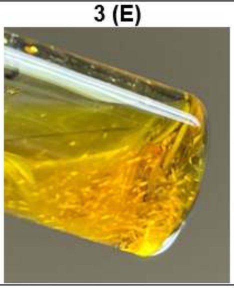
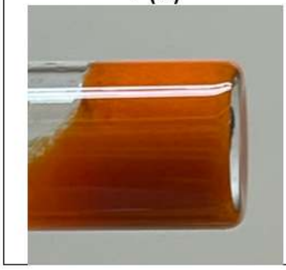
There are many alternatives, that can be used instead of the tested chemicals. Below, one might find a list of alternative chemicals suggested. However, **we recommend to test the alternatives** beforehand to confirm a chemical substitution. According to the chemical chosen, we recommend filling in the table with GHS hazard codes in the question text.

Chemical	Alternative(s)
 **1**	  vanillin 
 **3**	  citronellal 
 **4**	 
 **6**	 

Part B: Analysis of unknowns

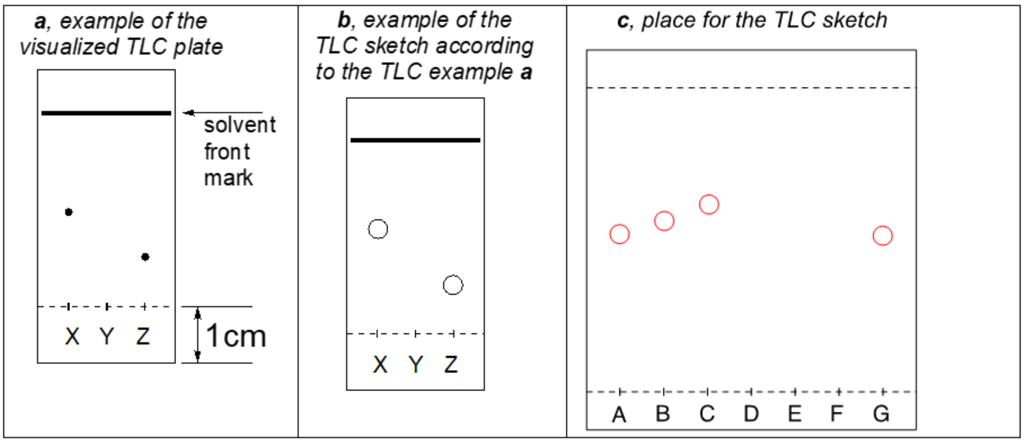
Q1: Note the observations in the table below.

Sample	A	B	C	D	E	F	G
Observation P – precipitate N – no precipitate	P	P	N	P	P	N	P

 1 (B)	 2 (A)	 3 (E)
 4 (D)	 5 (C)	 6 (F)
 7 (G)		

Q2: Sketch the TLC plate according to the example shown below.

The sketch of the TLC must be compared to the TLC observed as it may depend on the TLC plates and chemicals used.

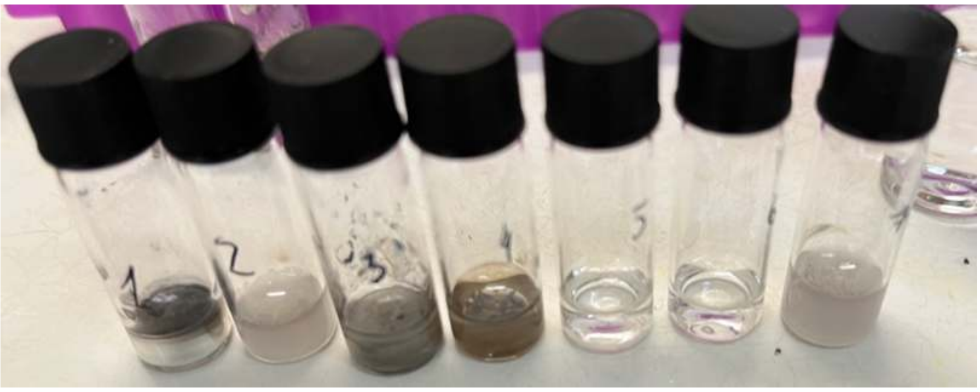


Q3: Note the observations in the table below.

Sample	A	B	C	D	E	F	G
Observation V – visible N – not visible	V	V	V	N	N	N	V

Q4: Write the observations in the table below. Note: A clear reaction should be observed. Repeat the experiment for the vials where the result is not clear enough.

Sample	A	B	C	D	E	F	G
Observation P – positive Tollens test N – negative Tollens test	N	P	N	N	P	N	N



Only in vials 1 and 3 the silver mirror is observed.

The overheating of the reaction mixture may lead to inferior results (below reaction with chemical 1 was performed three times; below, compare trials 1 and 2 to overheated trial 3). A weak silver mirror can be observed in case of 3, however, it is recommended to repeat the reaction to avoid errors.

Other compounds may give artefacts (small amount of grey precipitate, but not a mirror!) if overheated or/and not sufficiently pure. Therefore, we recommend to test the chemicals before the exam is given to students.

For the standard preparation of Tollens reagent refer to this source: https://edu.rsc.org/experiments/the-silver-mirror-test-with-tollens-reagent/822.article

Q5: Suggest the structure of unknown chemicals below. If some chemicals cannot be differentiated after the tests performed, write down all the possible numbers that can be assigned to chemicals.

Sample	A	B	C	D	E	F	G
Unknown	27	1	5	4	3	6	27

Q6: From the list below choose appropriate reagent(s) that can be used to figure out the remaining chemicals if any.

a) NaOH

b) NaOH, I_2

c) EtOH

d) $Na_2S_2O_3$, EtOH

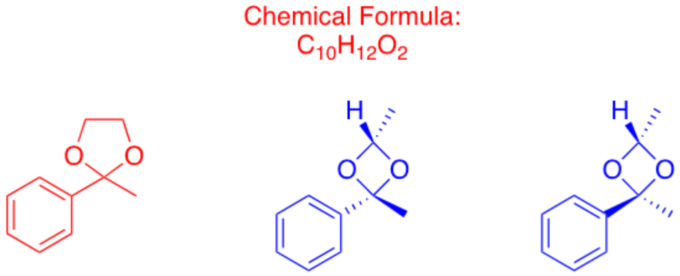
e) $(NH_4)_2[Ce(NO_3)_6]$, EtOH

f) $NaBH_4$, EtOH

Q7: Analyse the mass-spectra of the compounds **5** and **7** below and suggest possible structure(s) for them.

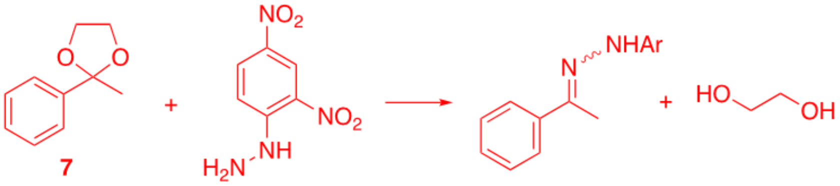
$PhCO_2Et$ is the only reasonable option for compound 5.

Dioxolane is the most probable option for 7 (red molecule), while dioxetanes are quite unstable (blue molecules).



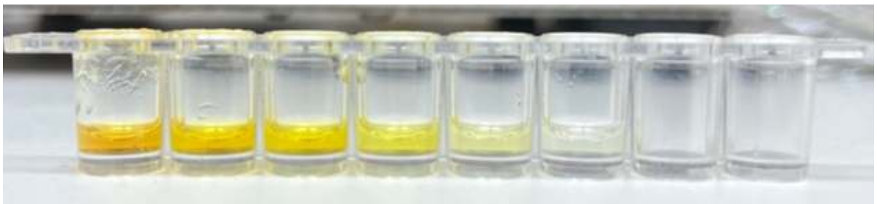
Q8.

5 + DNPH = no reaction



Part C: Analysis of DNPH concentration

Q9: Compare the concentration of the unknown DNPH sample with the concentration of the prepared DNPH solution, e.g. 5×c(prepared) < c(unknown) < 7 ×c(prepared).



It is recommended to perform this test and choose the most suitable concentration according to the biggest difference seen with the eye (in the test performed, the best concentration range was approximately c(prepared) = 150 × c(unknown)).

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