Data-based Questions (Organic Chemistry)

Instructions for Practice

These questions are data-based questions. You need to apply your knowledge to novel scenarios. Although the focus of this problem-set is on Organic Chemistry, other topics from H2 Chemistry are also included.

Usually, each question has a theme. The theme for each question is listed here, but it will be explicitly listed in your exams.

In Paper 2, data-based questions will take up about 20 to 25 marks of the paper. You should allocate slightly more time to solve these data-based questions. The ideal time allocation for each question is 1.5 minutes per mark.

All questions in this set are original, and it is most likely that you will be seeing these questions for the first time.

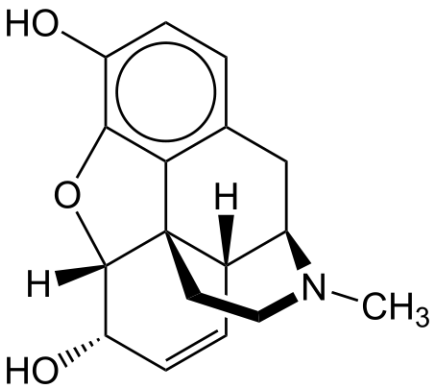
Happy revising!

Question number and Theme		Maximum Marks	Suggested time allocation
1	The synthesis of narcotics	20	35 minutes
2	Group 14 elements	20	35 minutes
3	All about archaea	25	42 minutes

1 Many illicit drugs found in the world are synthesised from naturally occurring organic compounds.

Known for its addictive properties, heroin is an illegal substance banned across the world. Heroin is not a natural product—it is produced from morphine found in opium.

The skeletal structure of morphine is provided below.



Morphine ($C_{17}H_{19}NO_3$)

(a) Stage 1: Extracting the morphine from raw opium

The raw opium was crushed. It was then mixed with hot water.

The composition was stirred until it became a homogenous suspension. The pH value was 8. Then calcium oxide was added, together with more hot water. The suspension was filtered, and the filtrate left to stand overnight. Further processes were made to ensure that more morphine was extracted from the residue.

To this filtrate, ammonium chloride was added. Solid morphine precipitated from the filtrate. The precipitate was collected through filtration.

(i) Write down **four** functional groups found in morphine. State the functional groups that contribute to the amphoteric nature of morphine. [3]

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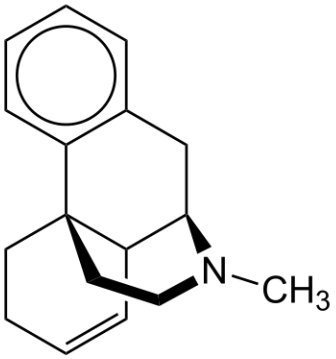
Questions by @ijustloveh2chem

(ii) Draw the predominant form of morphine after calcium oxide was added to the opium suspension. [1]

The carbon framework is given to you below.



(iii) Explain why after solid ammonium chloride was added, morphine precipitated from the filtrate. [2]

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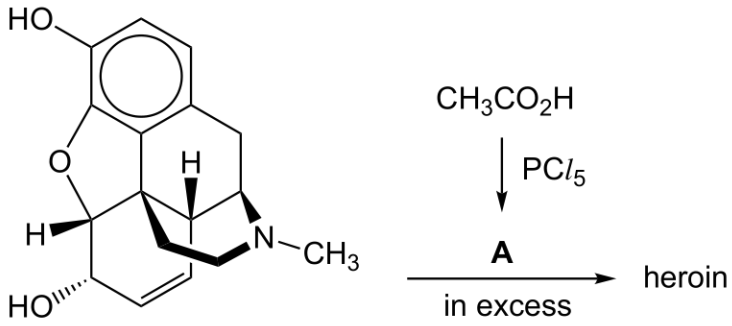
(b) Stage 2: Conversion of morphine to heroin

Heroin can be synthesised with Scheme 1.



Scheme 1

(i) Name **A**. [1]

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(ii) White fumes were reported to be evolved when heroin is synthesised using Scheme 1.

Name what constitutes the white fumes and hence explain why amateur drug makers do **not** use Scheme 1 to make heroin. [1]

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(iii) Instead of using **A**, amateur drug makers use acetic anhydride $(CH_3CO)_2O$.

After the reaction, sodium carbonate was added. Effervescence was observed, together with precipitation of heroin.

Suggest an equation to account for the effervescence. [1]

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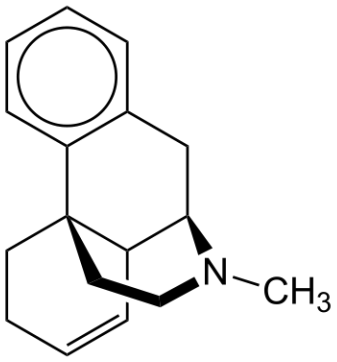
(iv) Heroin precipitated was filtered and retained. It was then washed and purified with aqueous ammonia. Finally, the purified heroin was dissolved in hydrochloric acid and a small amount of propanone. After evaporating the propanone, a white crystalline product was obtained.

Draw, with stereochemistry, the structure of this white crystalline product. [2]

The carbon framework is given to you below.



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(v) In a run to synthesise heroin, 3.9 kg of heroin (in the form of the white crystalline product in **(iv)**) was obtained from 7.8 kg of morphine.

Determine the percentage yield of heroin in this run. [2]

(vi) Heroin is more potent than morphine. When heroin is synthesised, small traces of unreacted morphine are still present in the heroin product. A higher purity of heroin often begs a higher price tag because it gives the user more pleasure with a smaller dose.

A drug dealer claims he has "pure heroin" in the powdered form.

Suggest a simple chemical test to examine whether the heroin is contaminated with morphine. [2]

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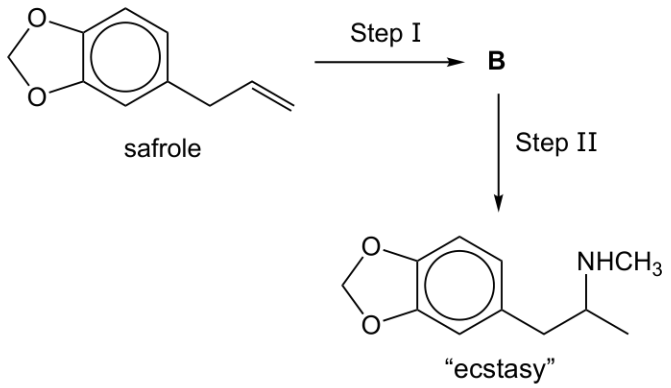
(c) "Ecstasy" is another illicit drug that can be synthesised from the naturally occurring compound safrole. Safrole can be found in Japanese star anise and the sassafras tree.



Scheme 2

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(i) Refer to Scheme 2. Suggest the reagent(s) and conditions for Step I, Step II and a structure for the intermediate **B**. [2]

Step I: …….

Step II: ……

B

(ii) Describe the mechanism for the conversion of **B** to "ecstasy". Indicate any relevant lone pairs and dipole moments clearly. [3]

[Total: 20]

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2 While carbon is an essential part of life, other Group 14 elements find important uses in organic chemistry and applications in everyday life.

(a) The mechanism regarding the hydrolysis of chlorosilanes was not widely known. However, kinetic studies were able to determine this mechanism.

Chlorosilanes have the general formula R_3SiCl. You may assume that the Si atom is sp^3 hybridised.

(i) Use the following facts to explain why the hydrolysis of chlorosilanes does **not** follow a S_N1 nor S_N2 type reaction.

- The relative rate of hydrolysis of SiX_4 (where X is a halogen) decreases as such: SiF_4, $SiCl_4$, $SiBr_4$, SiI_4. (Assume that the mechanism of the hydrolysis of SiX_4 is the same as the hydrolysis of chlorosilanes.)

- The overall order of reaction is three. [3]

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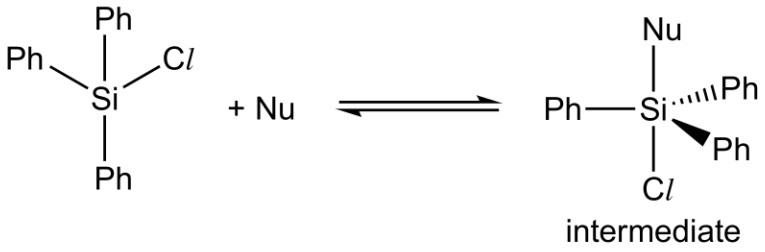
Step 1 of the hydrolysis of Ph_3SiCl (Ph = C_6H_5) is aided by a nucleophile, Nu. This is represented as an equilibrium with an equilibrium constant K_1.



intermediate

(ii) State the geometry at the Si atom of the intermediate. [1]

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(iii) In Step 2, the rate determining step, a water molecule coordinates onto the Si intermediate, forming a hexavalent Si complex. In the final step, the hexavalent Si complex decomposes quickly to form the hydrolysis product.

The rate law of step 2 is given by

$$\text{rate} = k_2 \text{ [intermediate] } [H_2O]$$

Show clearly that the overall order of reaction is three. [1]

(iv) When different nucleophiles are introduced, the observed rate constant of the reaction, k_{obs}, varies. Table 2.1 contains the observed rate constant for when 3 nucleophiles are present in separate runs.

Nucleophile (Nu)	k_{obs} / $dm^6\ mol^{-2}\ s^{-1}$
HMPA	1200
DMSO	50
DMF	6

Table 2.1

Deduce the relative nucleophilic strength of the three nucleophiles in Table 2.1. [1]

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(v) Suggest how the hydrolysis of Ph_3SiCl can exhibit second-order kinetics with respect to water. [1]

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(vi) Suggest a balanced equation for the hydrolysis of Ph_3SiCl. [1]

……

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(vii) Suggest a suitable solvent to study the kinetics of this hydrolysis reaction. [1]

……

(viii) Predict and explain how the relative rate of hydrolysis of $MePh_2SiCl$ (Me = CH_3) compares with Ph_3SiCl. [1]

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(b) Organotin compounds find good use in radical chemistry. Organic halides may be reduced into an alkane with the use of $^{n}Bu_3SnH$ ($^{n}Bu = CH_3CH_3CH_3CH_2$).

The mechanism of the reduction of bromomethane to methane is shown in Table 2.2. An initiator, AIBN, is added in step 1.

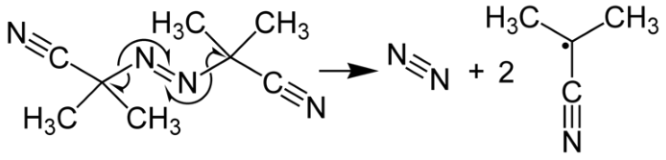
Step 1	
Step 2	
Step 3	$\bullet CH_3 + {}^{n}Bu_3SnH \rightarrow CH_4 + {}^{n}Bu_3Sn\bullet$
Step 4	

Table 2.2

Steps 2 to 4 are propagation steps.

(i) Complete Table 2.2 by suggesting balanced equations, with appropriate fish hook arrows, for steps 2 and 4. [3]

(ii) Suggest **two** possible termination steps. [1]

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(iii) Explain why only a small amount of AIBN is needed for the reaction to proceed. [1]

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(c) The valence shell of a Group 14 element has a pair of s electrons and 2 unpaired p electrons.

(i) Explain why the first ionisation energy of the elements in Group 14 generally decreases down the group. [1]

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(ii) Fill up Table 2.3 which presents the **cumulative** ionisation energies up to the second and fourth electron of tin and lead. [1]

cumulative ionisation energies up to the	2^{nd} electron	4^{th} electron
Sn	kJ mol^{-1}	kJ mol^{-1}
Pb	kJ mol^{-1}	kJ mol^{-1}

Table 2.3

(iii) The cumulative ionisation energies up to the fourth electron for Sn is lower than that of Pb. This difference is more marked when compared to the cumulative ionisation energies up the second electron. This may be explained with the *inert pair effect*, the phenomenon where the pair of s electrons is harder to remove in the later periods.

There are other relevant pieces of data from the *Data Booklet* which provide evidence of the *inert pair effect* in Group 14. These are the standard electrode potentials.

Quote only the relevant electrode potentials and use them to explain how this supports the *inert pair effect* for a Group 14 element. [3]

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[Total: 20]

Questions by @ijustloveh2chem

3 Archaea are microorganisms that can take unusual organic molecules as a source of energy. They are different from bacteria and other single-celled microorganisms.

(a) A nutrient medium containing only carbon-13 isotopically labelled methylamine, $^{13}CH_3NH_2$, in water can be hydrolysed, in the absence of oxygen, as an energy source with the presence of enzymes in certain species of archaea. Some gas was collected as metabolic products at room temperature. This gas contained 2 products in a 1:3 molar ratio. The relative molecular mass of the gas sample was 24.0. The only other non-gaseous product formed is NH_3.

It is known that the enzymatic hydrolysis of methylamine is a redox reaction.

(i) Determine the products of the gaseous mixture, given that there is no nitrogen atoms in the gas collected and both gaseous products contain at least a carbon atom. Identify the gas which was produced in greater amount. [3]

(ii) Hence, write a balanced equation for the enzymatic hydrolysis of methylamine. [1]

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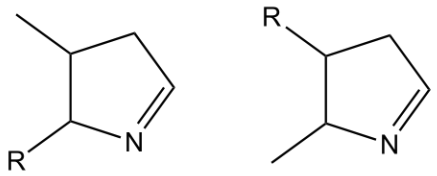
(b) Enzymes involved in methylamine utilisation in archaea contain the residue of an amino acid, **A**. That means that the partial hydrolysis of the enzymes can result in **A** being produced. The molecular formula of **A** is $C_{12}H_{21}N_3O_3$.

Through a series of enzymatic reactions, it is thought that **A** can be biosynthesised from 2 lysine molecules. The systematic name of lysine is 2,6-diaminohexanoic acid.

- Starting from lysine, enzyme 1 isomerises lysine to form **B**. **B** is a constitutional isomer of lysine.
- Amino acid **B** forms a peptide bond with lysine to form dipeptide **C**, catalysed by enzyme 2.
- Enzyme 3 converts **C** to **D**, in a process known as *oxidative deamination*[1]. **D** produces a brick-red precipitate when warmed with Fehling's reagent. The carbon backbones of **C** and **D** are the same.
- An intramolecular reaction results in **D** forming **A**. This is similar to the reaction where **D** produces a positive result with 2,4-DNPH.

Lysine, **A**, **B**, **C** and **D** are α-amino acids. When **A** is hydrolysed, a molecule of lysine is formed as one of its products.

A has a 5-membered ring. Instrumental analysis has narrowed down the carbon backbone of the ring of **A** to either **X** or **Y**. The R group is to be determined.



X **Y**

You may find this additional information useful in solving the question.

When 2 amino acids form a dipeptide, a new C—N bond is formed. This is known as a peptide bond. Fig 3.1 shows an example. The new C—N bond is in bold.

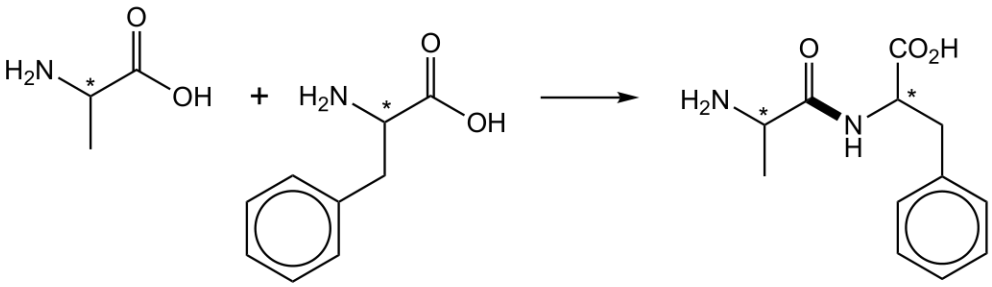


Fig 3.1

The asterisks (*) mark the α carbon of the two α-amino acids.

[1]*Deamination* is a reaction where a molecule loses an amine group.

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(i) Deduce the structure of the R group. [2]

(ii) Determine whether **A** has the carbon backbone of **X** or **Y**. You may find it useful to identify the α carbons in **A** first. [1]

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……

(iii) Deduce the structures of **B**, **C** and **D**. For each reaction in the bullet points, state the type of reaction described and the functional group involved. [5]

Questions by @ijustloveh2chem

The cell membrane of archaea is composed of a lipid bilayer similar to bacteria. However, there are a few structural differences in the lipids found in cell membranes. Table 3.2 shows the structural formula of the lipids.

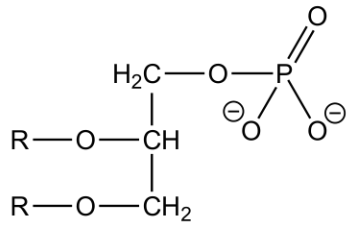	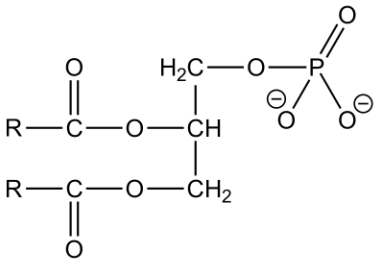
Structure of the lipids found in archaea	Structure of the lipids found in bacteria

Table 3.2

In part **(c)**, the R group is a long hydrocarbon chain, and differs between species of archaea and bacteria. The R group in **(b)** is not to be considered in subsequent parts.

(c) **(i)** From Table 3.2, state **one** difference between the structure of the lipids found in archaea and bacteria. [1]

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The lipid bilayer may act as a "liquid" or "solid" depending on the temperature. At the phase transition temperature, the lipid bilayer may transition from the "liquid" to the "solid" phase (or *vice versa*). The phase transition temperature is attributed to the strength of the interactions between the R groups.

(ii) State the predominant interactions between the R groups of the lipids and explain how they arise. [2]

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(iii) The R groups found in archaea are typically branched and contain rings. However, the R groups found in bacteria are typically straight chain hydrocarbons.

Suggest why the phase transition temperature of archaea is generally lower than that of bacteria. [1]

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(iv) The presence of unsaturation in the R group affects the phase transition temperature due to the disruption of packing between individual lipid molecules. This may be attributed to "kinks" in the R group. "Kinks" are inflexible bends in the R group.

Explain why "kinks" are inflexible. [1]

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(v) Suggest another characteristic of the R group, other than that discussed in **(iii)** and **(iv)**, that will affect the phase transition temperature of the lipid bilayer in both and bacteria and explain your answer. [2]

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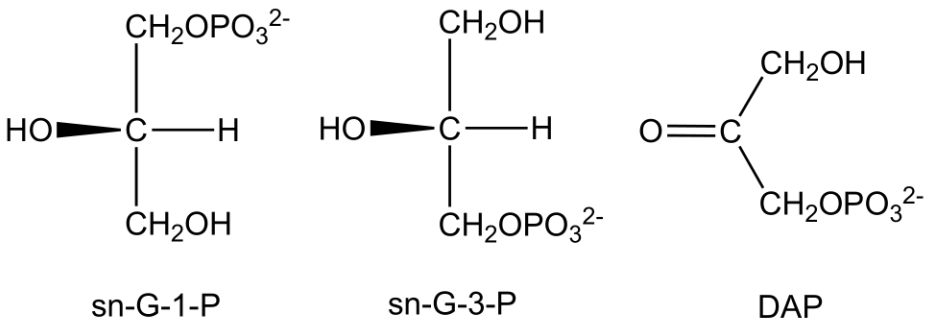
(d) Lipids have a glycerol backbone and are biosynthesised from a glycerol phosphate precursor. In bacteria, the template glycerol phosphate is sn-G-3-P while the template glycerol phosphate is sn-G-1-P for archaea. Both sn-G-3-P and sn-G-1-P come from dihydroxyacetone phosphate (DAP). The structures of sn-G-3-P, sn-G-1-P and DAP are shown below.



sn-G-1-P sn-G-3-P DAP

Questions by @ijustloveh2chem

(i) DAP is reduced by NADH to form sn-G-3-P or sn-G-1-P depending on reaction conditions. The oxidised form of NADH is NAD^+.

Standard reduction potentials are quoted in Table 3.3.

Couple	Half-equation	$E^\ominus$ / mV
DAP / sn-G-3-P		−190
NAD^+ / NADH	$NAD^+ + H^+ + 2e^- \rightleftharpoons NADH$	−320

Table 3.3

Complete the half equation for the reduction of DAP to sn-G-3-P. [1]

You may use the abbreviations DAP and sn-G-3-P.

(ii) Show that the reduction of DAP to sn-G-3-P by NADH is spontaneous, and calculate $\Delta G^\ominus$ of the process per mole of DAP reduced to sn-G-3-P. [2]

(iii) Explain how the presence of enzymes that catalyse the reaction affects the standard cell potential of the reduction of DAP by NADH. [1]

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(iv) Compare $E^\ominus$(DAP / sn-G-1-P) with $E^\ominus$(DAP / sn-G-3-P). Explain your answer. [1]

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Questions by @ijustloveh2chem

(v) A hydroxyl (—OH containing) organic compound that has a long hydrocarbon chain, together with sn-G-1-P or sn-G-3-P, are combined to form the lipid bilayer in bacteria and archaea. This process is facilitated by enzymes which catalyse the biosynthesis of the lipid bilayer.

The stereochemical configuration of the template glycerol phosphate is retained.

Fig 3.4 illustrates an example for the biosynthesis of the lipid bilayer for archaea.

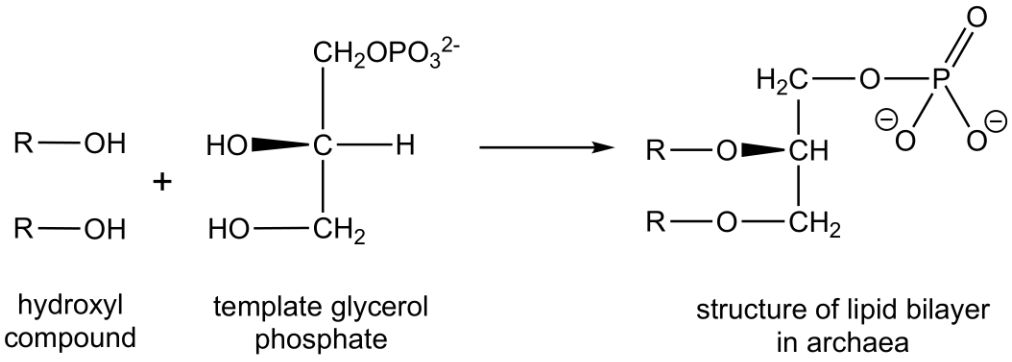

Fig 3.4

Using the information above, redraw the **displayed formula** of the lipid bilayer for bacteria. You must indicate stereochemical information where relevant. [1]

Your answer should retain the same functional groups as shown in Table 3.2.

[Total: 25]

Questions by @ijustloveh2chem