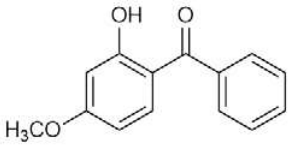
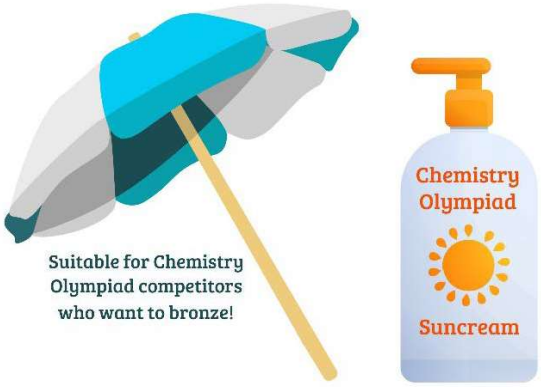
3. This question is about sun cream

On 1st January, the Pacific island of Palau imposed a ban on certain sun creams to protect its coral reefs. The ban restricts the use of ten products which are toxic to marine life and are linked to the bleaching of coral. Scientists are particularly concerned with two UV light-absorbing chemicals: oxybenzone and octinoxate.



oxybenzone



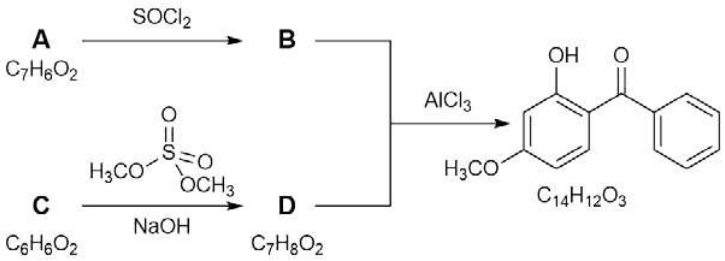
(a) Which functional groups are present in oxybenzone? Tick the correct answer(s) in the answer booklet.

ester	aldehyde	ketone
carboxylic acid	ether	phenol

Oxybenzone is good at absorbing UV radiation due to the delocalisation of its electrons. This delocalisation of electrons is aided by an **intra**molecular hydrogen bond in oxybenzone.

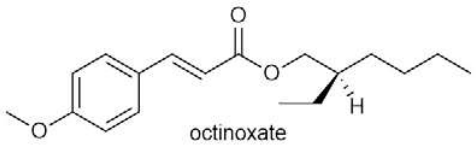
(b) On the oxybenzone structure in the answer booklet, circle the two atoms involved in the **intra**molecular hydrogen bond.

The synthesis of oxybenzone is shown below.



(c) Draw the structures of compounds **A**, **B**, **C** and **D**.

Octinoxate exists as multiple stereoisomers; only one is shown. Enantiomers are stereoisomers that are non-superimposable mirror images of each other.

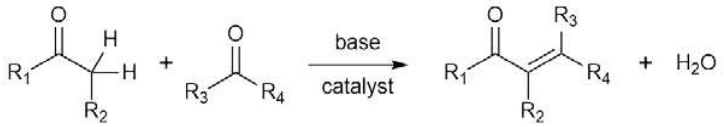


octinoxate

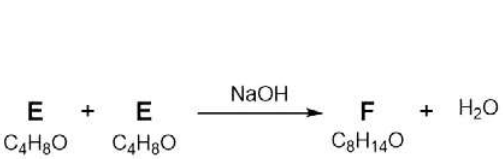
(d) **(i)** Draw a second stereoisomer of octinoxate that is the enantiomer of the one shown.

(ii) Draw a third stereoisomer of octinoxate that is not the enantiomer of the one shown.

In the synthesis of octinoxate, a base-catalysed condensation reaction between two molecules containing C=O groups is used. The product of this reaction is a molecule that contains a C=C and a C=O bond next to each other. This proximity helps to make octinoxate a good absorber of UV light.



The synthesis of octinoxate begins with the conversion of two molecules of **E** to **F**.

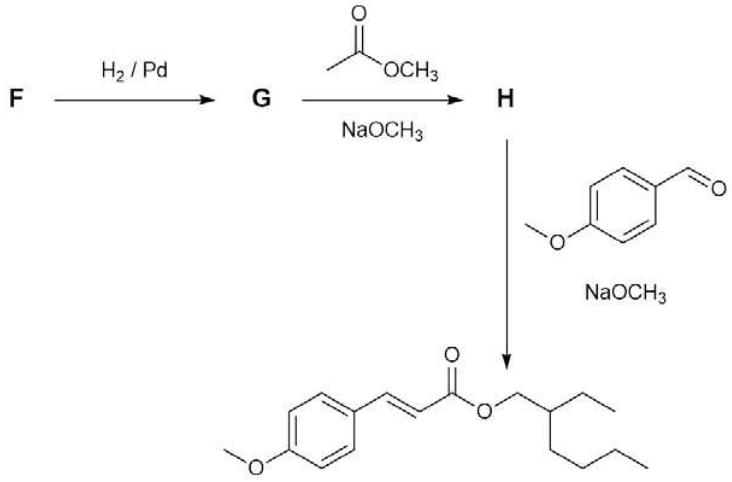


E: IR: 1730 cm^{-1}
^1H NMR: 0.9 ppm, 3H, triplet
1.6 ppm, 2H, multiplet
2.5 ppm, 2H, multiplet
9.7 ppm, 1H, triplet

F: IR: 1628 cm^{-1}
1687 cm^{-1}

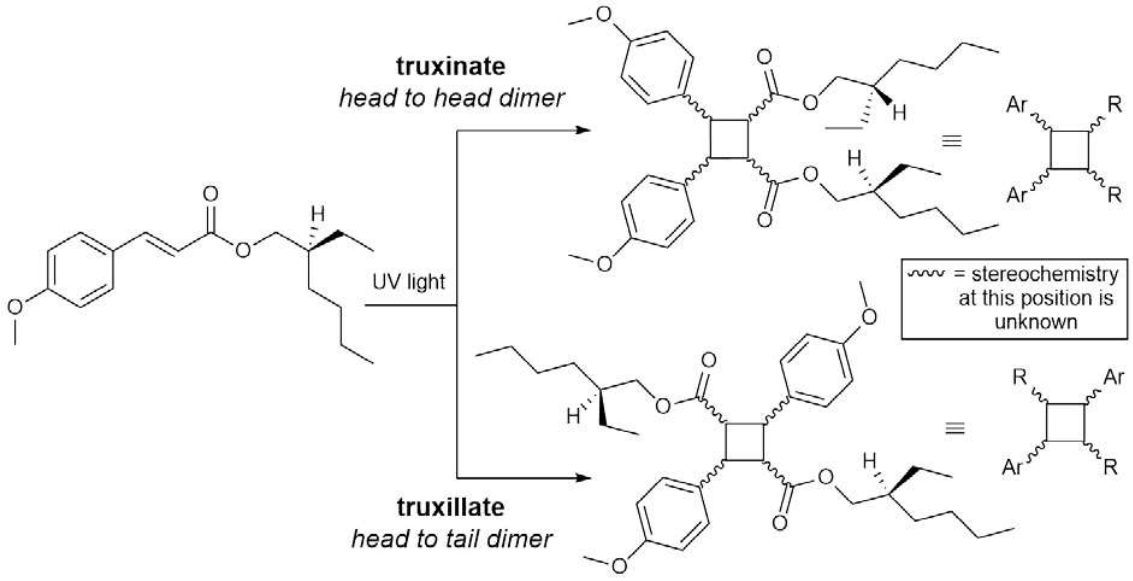
(e) Draw the structures of compounds **E** and **F**. Stereochemistry is not required.

Compound **F** is then converted into octinoxate in three steps. By-products are not shown.



(f) Draw the structures of compounds **G** and **H**. Stereochemistry is not required.

Upon exposure to UV light, octinoxate forms two types of dimers which are toxic to marine life: truxinates and truxillates. If a single stereoisomer is irradiated with UV light, many different truxinate and truxillate stereoisomers can be formed due to the position of the groups (abbreviated as R or Ar) on the newly formed cyclobutane ring.



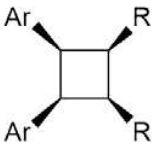
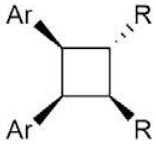
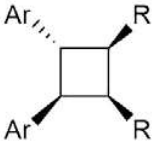
(g) What do all the truxinate and truxillate products produced in this reaction have in common? Tick the correct answer(s) in the answer booklet.

The same molecular formula

The same melting points

Rotate plane-polarised light in the same direction

A research group separated the products formed to further understand their toxicological properties. The truxinate dimers can be categorised by the number of substituents on the same face of the cyclobutane ring (either two, three or four). This is shown with wedged and hashed bonds.

Substituents on same face	Truxinates	
Four		
Three		

(h) **(i)** In the answer booklet circle to indicate whether each structure has an enantiomer.

(ii) In the answer booklet, draw the structures to complete the '**Two**' line(s) in the table. Indicate whether each structure has an enantiomer. For a pair of enantiomers, only draw one of the pair. Not all boxes need to be used.