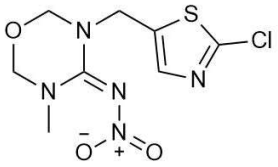
4. This question is about bees and Brexit

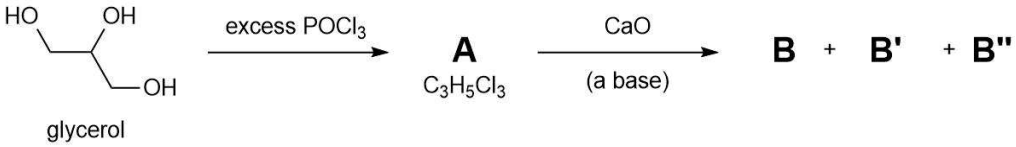
There is concern that neonicotinoid pesticides are harmful to bees. Thiamethoxam is one of three neonicotinoids that the European Union (EU) banned from all outdoor uses in April 2018. When Britain leaves the EU, this pesticide may become available for use in the UK again. People are worried this will harm our bee population.



thiamethoxam

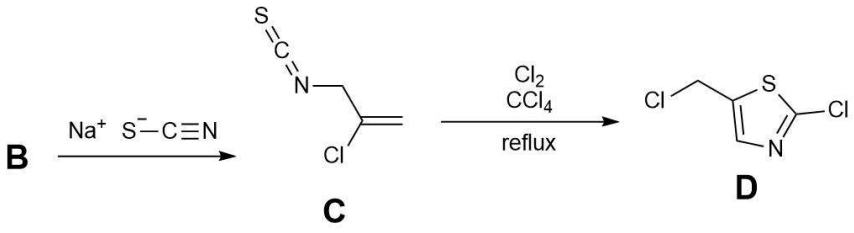
(a) What is the molecular formula of thiamethoxam?

The synthesis of thiamethoxam begins with glycerol. In the conversion of **A** to **B**, two other side products (**B'** and **B''**) can also be formed. **B**, **B'** and **B''** are isomers. **B'** and **B''** are geometric isomers. Much less **B''** is formed than **B'**.



(b) Draw the structures of **A**, **B**, **B'** and **B''**.

B reacts with sodium thiocyanate (NaSCN) to form **C**, which can be converted into **D** upon treatment with chlorine and carbon tetrachloride.

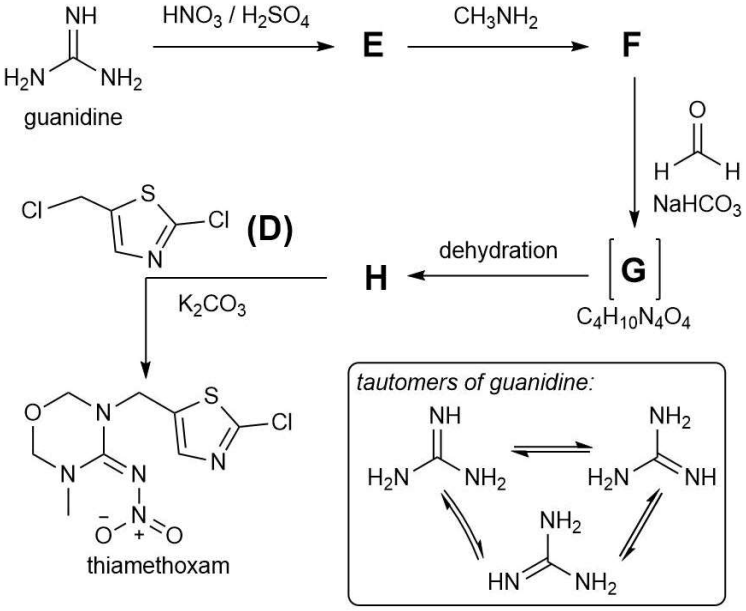


(c) Draw a resonance structure of the thiocyanate ion that explains the formation of **C**.

The remainder of the synthesis begins with guanidine.

Guanidine exists as one of three equivalent tautomers, which are all in rapid equilibrium with each other. Tautomers are isomers that only differ in the position of hydrogen atoms and double bonds.

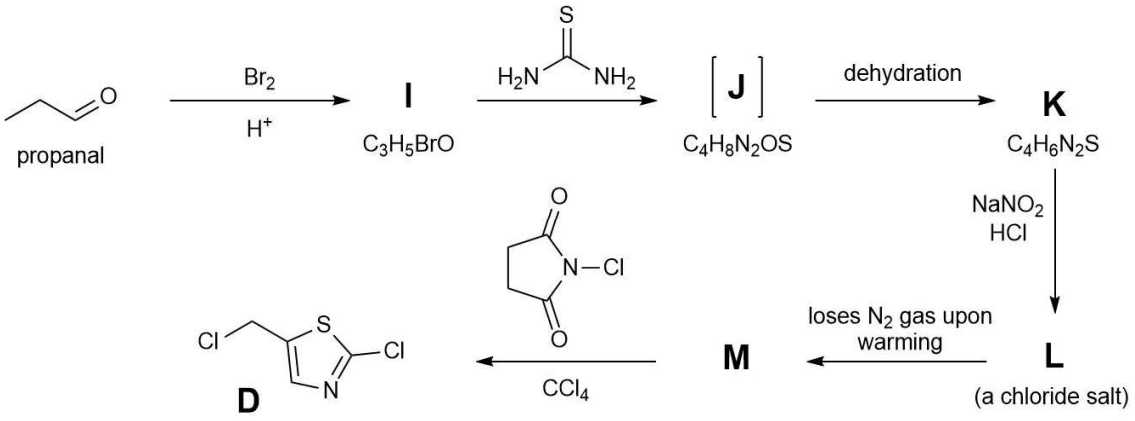
Each intermediate (**E**, **F**, **G** and **H**) can also exist as different tautomers.



(d) Draw the electrophile that reacts with guanidine to form **E**, clearly indicating its shape.

(e) Draw the structures of **E**, **F**, **G** and **H**. You only need to draw one tautomer for each compound.

In an alternative synthesis of thiamethoxam, compound **D** can also be synthesised from propanal.



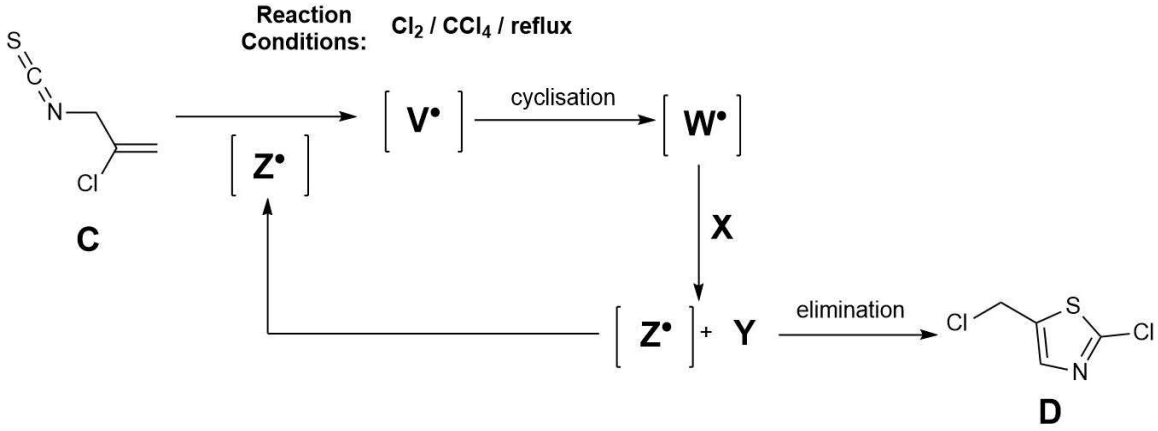
(f) Draw the structures of **I** and intermediate **J**.

Intermediate **J** undergoes dehydration to form **K**. There are three possible tautomers of **K**. However, as one tautomer is aromatic (as it has six π electrons in a ring like benzene), this tautomer is far lower in energy than the other two. Hence, at equilibrium this lowest energy tautomer predominates.

(g) Draw the structure of the lowest energy tautomer of **K** (showing the π electrons as double bonds rather than as a circle).

(h) Draw the structures of **L** and **M**.

The conversion of **C** to **D** occurs via a free radical chain reaction, followed by an elimination. The chain-carrying radical **Z·** adds to the thiocyanate in **C** to give radical intermediate **V·**. Intermediate **V·** undergoes cyclisation to give radical intermediate **W·**, which reacts with reagent **X** to form **Y** and regenerate the chain-carrying radical **Z·**. **Y** then undergoes an elimination to form **D**.



(i) Draw the structures of radical intermediates **V·** and **W·**, and intermediate **Y**.

(j) Identify reagent **X** and chain-carrying radical **Z·**.