'Asparagus pee'

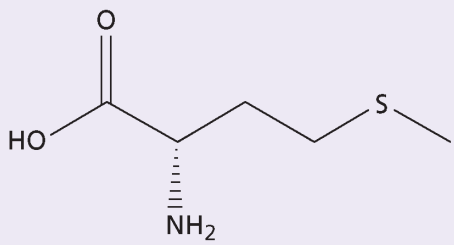
Asparagus

Do you eat asparagus, and if so do you notice a particular unpleasant smell in your urine some time afterwards? If so you are not alone – between 1/3 and 1/5 of the population notice this smell. It seems probable that sulfur-containing amino acids such as methionine are broken down in the body to other sulfur-based compounds. These, like many sulfur-containing compounds, have an unpleasant smell. (Hydrogen sulfide, H_2S, is the compound that causes the smell of bad eggs.)

The reason that not everyone can smell 'aspragus-pee' is the subject of debate. Scientists remain divided on why people have different urinary responses to eating asparagus. One camp thinks only about half of the population have a gene enabling them to break down the sulfur-containing amino acids in asparagus into their smellier components. Others think that everyone digests asparagus the same way, but less than half of us have a gene that enables us to smell the specific compounds formed in the digestion of asparagus.

Questions

1. The amino acid methionine has the formula



   Perhaps surprisingly the amino acid asparagine contains no sulfur. Find out the names and formulae of the two other naturally-occurring amino acids that contain sulfur.

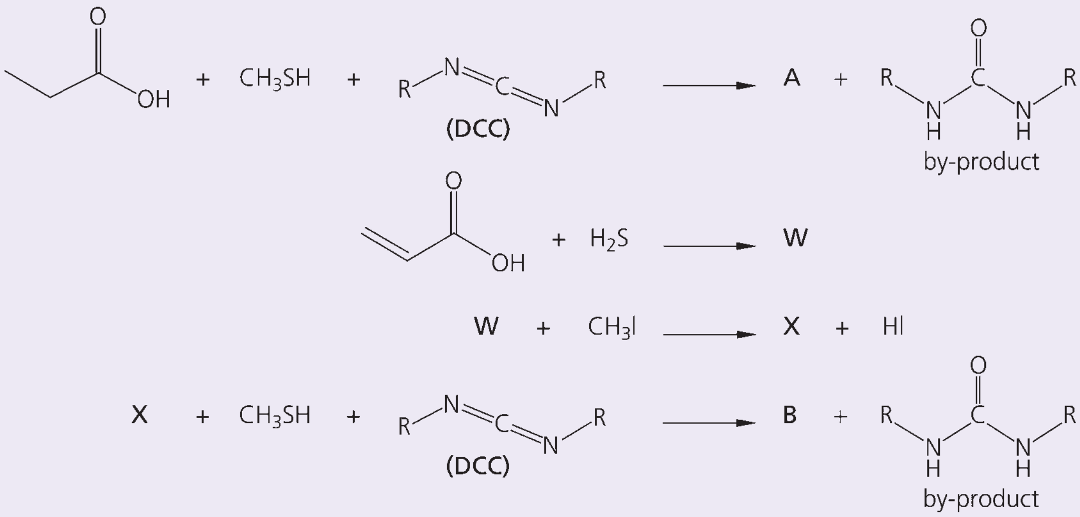
2. This question is about 'asparagus-pee'.

   It has long been known that after eating asparagus, many people can detect an odd odour in their urine. (Whether or not a person can actually smell it is apparently genetic.)

In the 19th century it was thought that the compound responsible for the smell in so-called 'asparagus-pee' was methanethiol, CH_3SH.

In a more recent study, no methanethiol was detected in the vapour from asparagus-pee but two other sulfur-containing compounds, **A** and **B**, were identified by mass spectrometry. The M^+ ion for compound **A** is at *m/e* = 102; for compound **B**, *m/e* = 150.

For comparative purposes, compounds **A** and **B** were also prepared in the laboratory from propenoic acid by the following routes.



Compound **A** reacts with HBr to give **Y** and with Br_2 to give two isomers, **Z1** and **Z2**.

Y is not optically active and has two peaks for its M^+ ion at *m/e* = 182 and 184 (1:1 ratio).

Z1 and **Z2** are enantiomers (optical isomers) and their M^+ ions have *m/e* = 260, 262, and 264 (ratio 1:2:1).

(a) State the role of the reagent 'DCC':
i) catalyst; ii) hydrating agent; iii) dehydrating agent; iv) hydrogenating agent or
v) dehydrogenating agent.

(b) Suggest structures for compounds **A, B, W, X, Y, Z1,** and **Z2**.

(c) Both **A** and **B** may be hydrolysed in water, releasing methanethiol (hence the earlier suspicion of this compound).

Write balanced equations for the hydrolysis reactions of both **A** and **B**.

[Naturally occurring bromine is a 1:1 mixture of ^{79}Br and ^{81}Br]