29.2 CHARACTERISTIC ORGANIC REACTIONS

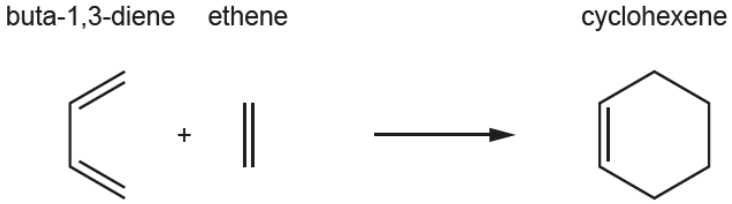
Learning outcomes

Candidates should be able to:

1. Understand and use the following terminology associated with types of organic mechanisms:
   (a) electrophilic substitution
   (b) addition–elimination

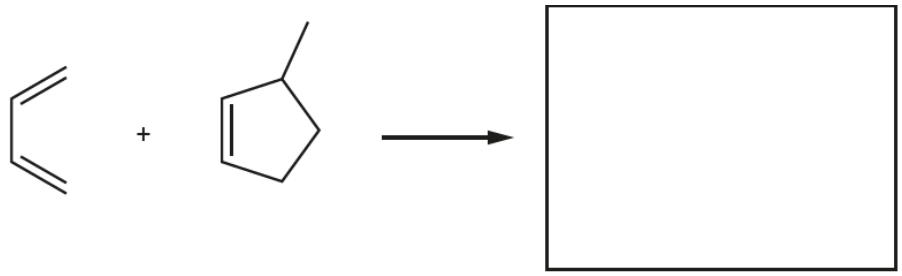
Introduction

1. Some syntheses use Diels–Alder reactions, which normally involve a diene and an alkene reacting together to form a cyclohexene.
   (i) Draw three curly arrows in Fig. 9.4 to complete the mechanism for the Diels–Alder reaction between buta-1,3-diene and ethene. [1]



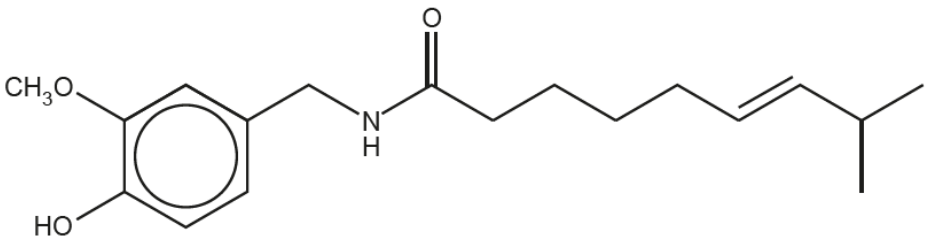
   (ii) Another Diels–Alder reaction of buta-1,3-diene is shown in Fig. 9.5.
   Predict the product formed in this reaction. [1]

2.



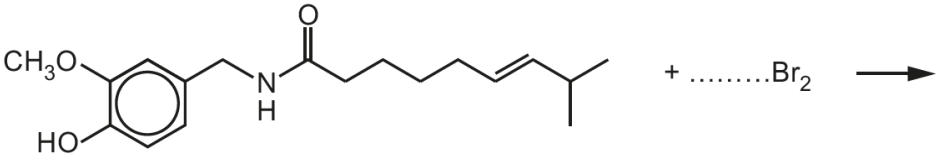
3. Capsaicin is found in chilli peppers.

capsaicin



   Complete the equation for the reaction of capsaicin with an excess of $Br_2(aq)$ in the dark.
   Draw the structure of the organic product in the labelled box. [3]

capsaicin



organic product

+ .....

4. Capsaicin is heated with an excess of hydrogen gas in the presence of platinum metal.
The six-membered ring reacts in the same way as benzene under these conditions.
Draw the structure of the organic product formed. [2]

5. When capsaicin is treated with reagent J under suitable conditions, one of the products is methylpropanoic acid, $CH_3CH(CH_3)COOH$.
(i) Identify reagent J and any necessary conditions.

..... [1]

(ii) There are three different peaks in the proton (1H) NMR spectrum of $CH_3CH(CH_3)COOH$ in $CDCl_3$.
Table 8.1

environment of proton	example	chemical shift range δ / ppm
alkane	$-C\mathbf{H}_3$, $-C\mathbf{H}_2-$, $>C\mathbf{H}-$	0.9–1.7
alkyl next to C=O	$C\mathbf{H}_3-C=O$, $-C\mathbf{H}_2-C=O$, $>C\mathbf{H}-C=O$	2.2–3.0
alkyl next to aromatic ring	$C\mathbf{H}_3$–Ar, $-C\mathbf{H}_2$–Ar, $>C\mathbf{H}$–Ar	2.3–3.0
alkyl next to electronegative atom	$C\mathbf{H}_3$–O, $-C\mathbf{H}_2$–O, $-C\mathbf{H}_2-Cl$	3.2–4.0
attached to alkene	=C**H**R	4.5–6.0
attached to aromatic ring	**H**–Ar	6.0–9.0
aldehyde	**H**COR	9.3–10.5
alcohol	RO**H**	0.5–6.0
phenol	Ar–O**H**	4.5–7.0
carboxylic acid	RCOO**H**	9.0–13.0

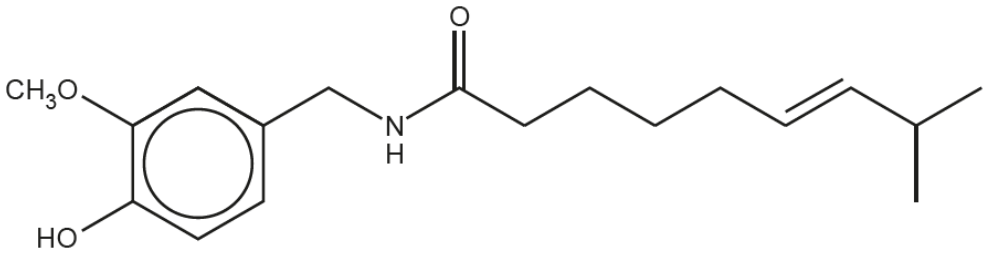
6. Use Table 8.1 to complete Table 8.2 and state:
- the typical proton (1H) chemical shift values (δ) for the protons
- the splitting pattern (singlet, doublet, triplet, quartet or multiplet) shown by each peak
- the explanation for the splitting patterns of the CH_3 protons and the CH proton.

Table 8.2

environment	δ / ppm	splitting pattern	explanation for splitting pattern
CH_3			
CH			
COOH			

7. Capsaicin is heated with an excess of hot aqueous NaOH.

capsaicin



Draw the structures of the two organic products H and K. [2]

H $C_8H_{10}NO_2Na$

K $C_{10}H_{17}O_2Na$

(ii) Name the two types of reaction occurring in (e)(i).

..... [1]

(f) Draw the structure of the organic product L formed when capsaicin is treated with LiAl H4 in dry ether. [1]

L