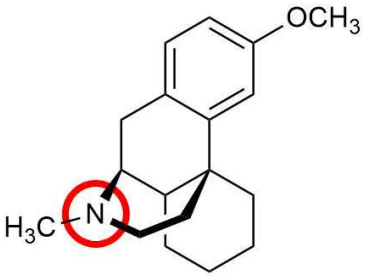
4. This question is about cough suppressants

(a)



1

Note: The hydrogen at the central ring junction which is drawn later in the question to indicate the stereochemistry has been omitted here to avoid confusing students.

(b) Molecular formula of dextromethorphan = $C_{18}H_{25}NO$ **1**

Molecular formula of hydrobromide monohydrate salt = $C_{18}H_{25}NO + H_2O + HBr$

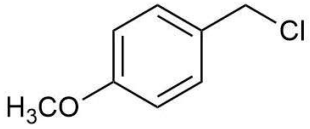
$= C_{18}H_{28}BrNO_2$

Molar mass = $[(18 \times 12.01) + (28 \times 1.008) + 79.904 + 14.01 + (2 \times 16.00)]$ g mol^{-1}

= 370.318 g mol^{-1} **1**

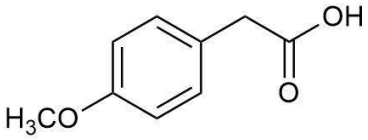
1 mark for correct determination of molecular formula of dextromethorphan, 1 mark for final answer.

(c) **Compound A**



1 mark

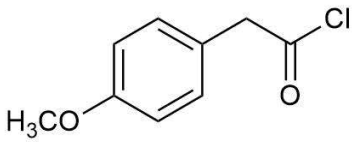
Compound B



1 mark

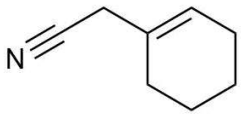
2

Compound C



1 mark

Compound D

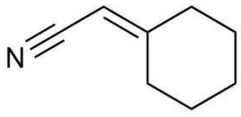


2 marks

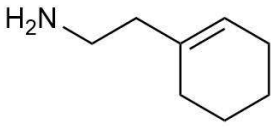
3

Nitrile group does not have to be drawn out.

The following incorrect isomer scores 1 mark.



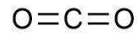
Compound E



1 mark

No credit awarded if alkene is in wrong position.

Gas X



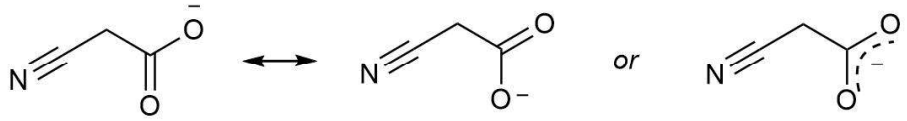
1 mark

Accept if structure is not drawn out or carbon dioxide is written in words.

2

*ECF can be awarded for compounds **B** and **C** only. It cannot be awarded for the others because there is a known compound to work forward from or back from. An example where ECF could be used for compound **B** or **C** is in the case of a small error such as an extra CH_2 in the chain.This should of course be penalised when it first occurs (in compound **A** for example), but ECF can be awarded if the rest of the chemistry in **B** and/or **C** is correct after the initial mistake.*

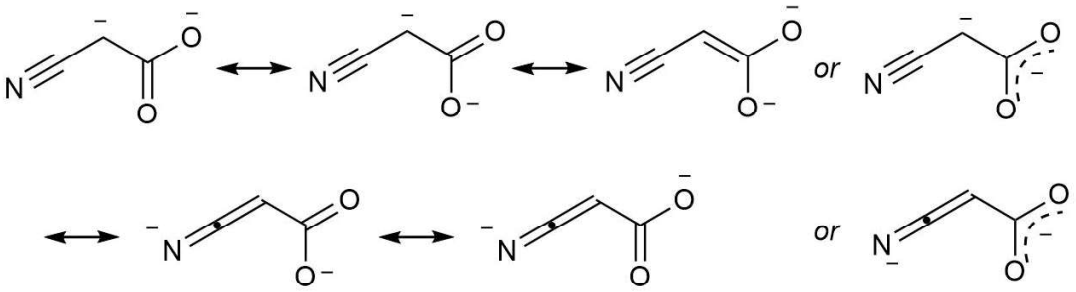
(d) (i) **Anion Z^-**



1

Only one correct form is required to score the mark.

(ii) **Dianion Z^{2-}**



1

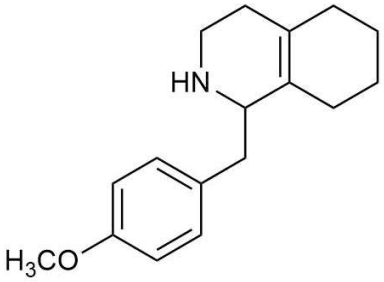
Only one correct form is required to score the mark.

(e) 9 and 13

1

½ mark each

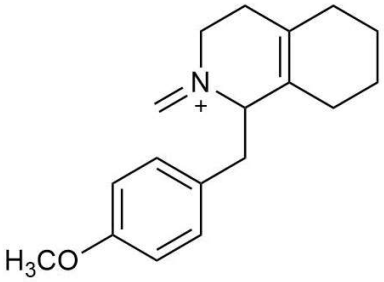
(f) **Compound H**



1 mark

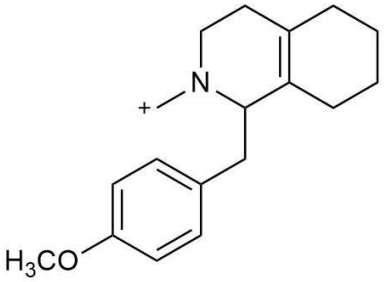
No credit if the incorrect double bond is reduced.

Cation I^+



2 marks

Also accept for 2 marks



*ECF can be awarded if a trivial mistake in Compound **H** (such as an extra CH_2) is repeated here.*

3

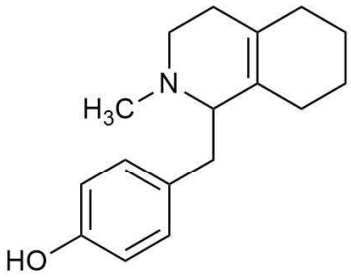
(g) 4 and 13 **1**

4 and 15 **1**

One mark to be awarded for each complete pair. If the pair is not correct then no partial credit can be scored (e.g. 4 and 7 does not score any credit). If three pairs are written down the maximum score is 1 mark if there is at least one correct pair. If four or more pairs are written down then the score is zero.

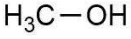
*When discussing with students afterwards please point out that it is the symmetry present in the benzene ring that means that there are two possible pairs of carbon atoms that can become connected. It is NOT the case that connecting one pair makes isomer **M_1** and the other one **M_2**. Which of compound **M_1** or **M_2** is formed depends on which face of the alkene in intermediate **K** is protonated to make carbocation **L^+** (protonation on one face gives **M_1** and protonation on the other face gives **M_2**).*

(h) **Intermediate K**



1 mark

Liquid Y

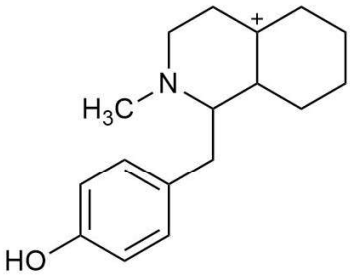


1 mark

Accept if not drawn out as a structural formula or methanol is written in words.

2

Carbocation L^+

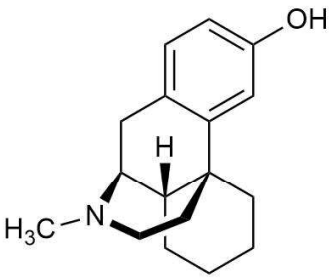


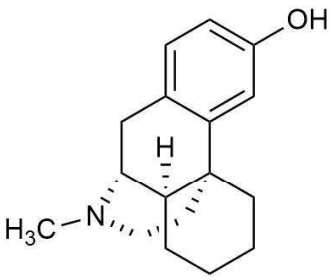
2

*If positive charge is not in correct position then no marks can be awarded. ECF can be awarded if an error in intermediate **K** (such as not removing the methyl group, or removing the methyl group on the nitrogen rather than the oxygen) is also present here.*

When going through this paper with students afterwards you should draw an analogy to the more familiar Friedel–Crafts alkylation reactions which proceed via similar carbocations reacting with electron-rich benzene rings.

(i) **Compound M_1** **Compound M_2**





2

1 mark *1 mark*

*Compounds **M_1** and **M_2** can be either way around. The stereochemistry of the bond to nitrogen and the bond to carbon must be clearly shown for the mark in each case These two substituents must be shown to be above the plane of the rings in one isomer and below the plane of the rings in the other isomer. The stereochemistry of the hydrogen does not need to be shown, but if shown must be correct or half a mark should be deducted in each structure. A structure where one of the carbon/nitrogen substituents is up and the other is down scores no marks.*

*ECF can be awarded if an error in intermediate **K** (such as not removing the methyl group, or removing the methyl group on the nitrogen rather than the oxygen) is also present here.*

Type of isomers: **Enantiomers** **1**

Allow 'optical isomers'. Award ½ mark for 'stereoisomers' (as whilst this is true we can be more specific here as the two compounds are enantiomers).

Question Total 25