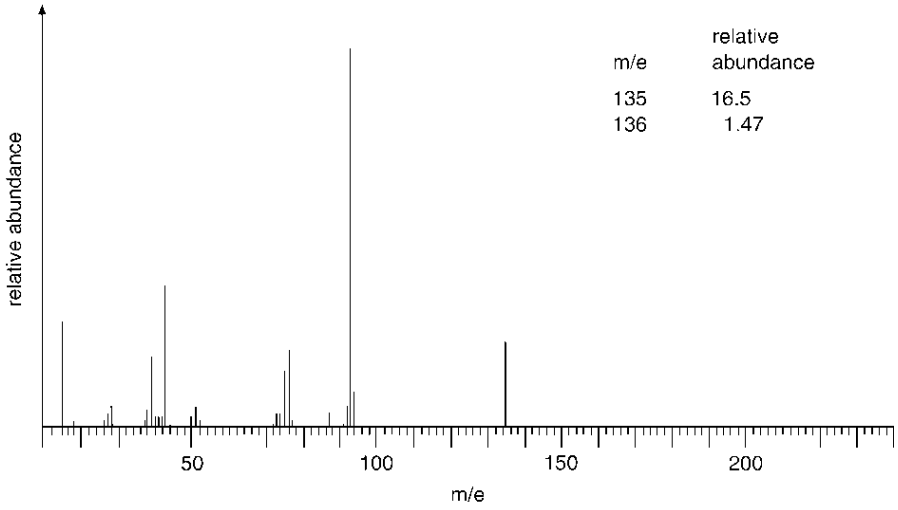
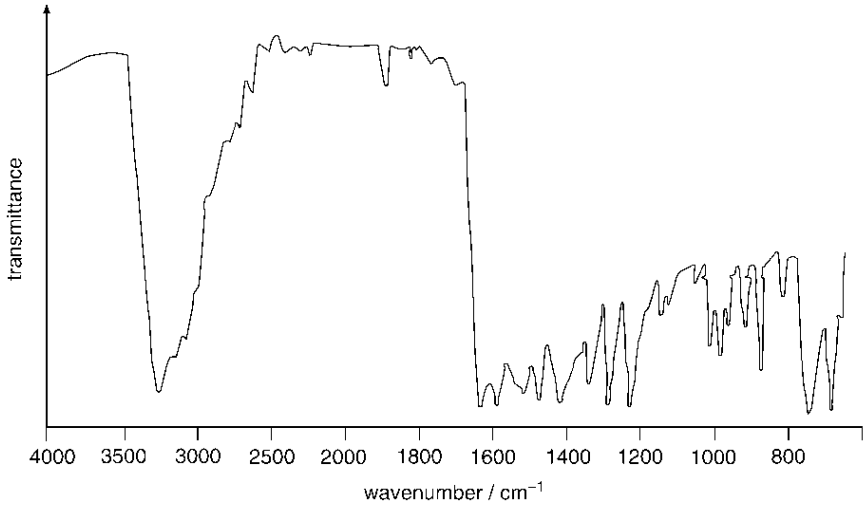
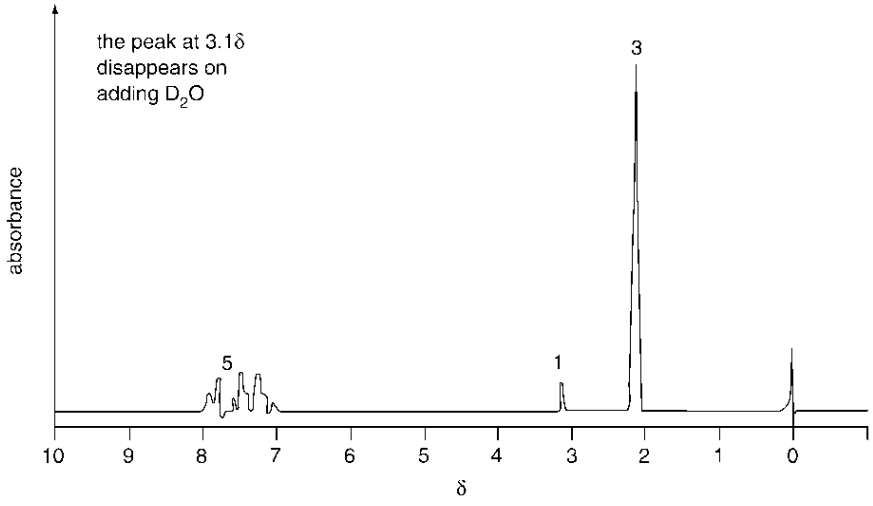
Anderson Serangoon Junior College
2025 H3 Chemistry
Interpretation of Spectra

1 The spectra shown below were obtained from compound **Q**, which contains the element carbon, hydrogen, nitrogen and oxygen.

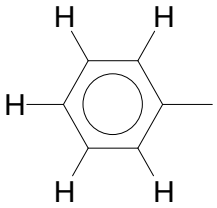
Consider the NMR, mass and IR spectra in turn. Explain what information each spectrum gives about **Q**. Hence give a possible structure for the compound.







NMR

δ /ppm	Multiplicity	No of H	Deduction
7-8	Multiplet	5	 Monosubstituted phenyl ring
2.1	Singlet	3	-C**H**$_3$ with no H on adjacent C
3.1	Singlet	1	Since the peak disappear on adding D_2O, it is a labile proton, attached to an electronegative atom.

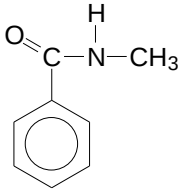
MS

M : M+1
16.5 : 1.47
100 : 1.1 n

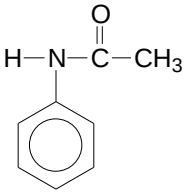
No. of carbon atoms = (100/1.1)(1.47/16.5) = 8

Given Q contains C, H, O and N,
Peak at m/e 135 could be molecular ion $C_8H_9NO^+$.

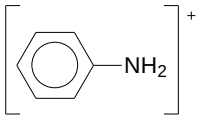
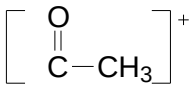
Structure of Q could be A or B.



A



B

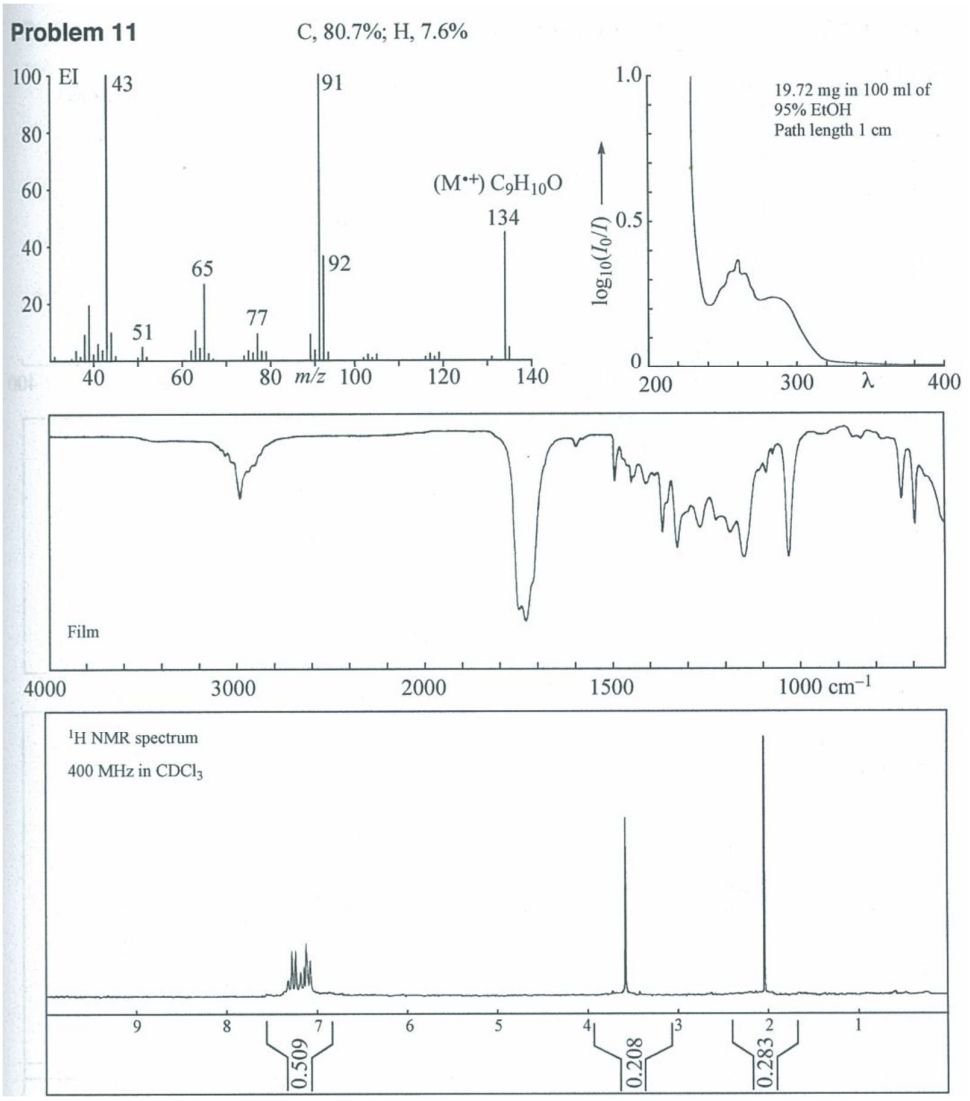
m/e		Fragment
93	135 – 42	
43	-	

Absence of m/e at 105 suggest absence of $C_6H_5CO^+$.
From the fragment ions, structure of Q is **B**.

IR

Presence of N-H at 3300 cm^{-1}
Prsence of amide functional group.

2 Interpret the following spectra and use them to suggest a structure for the unknown compound.



MS
peak at m/e 91 is $[C_6H_5CH_2]^+$ (benzyl or tropilium cation)
peak at m/e 77 is $[C_6H_5]^+$
peak at m/e 43 is $[CH_3CO]^+$

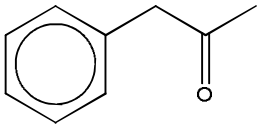
UV/VIS
Compound shows several absorptions within UV/VIS region, suggesting presence of a conjugated π-system

IR
C-H stretch at 3100cm^{-1}
Strong absorption at 1750cm^{-1} due to C=O stretch.

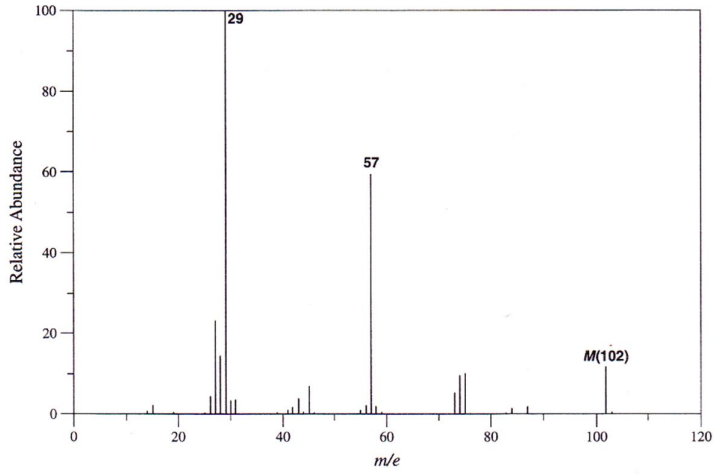
NMR

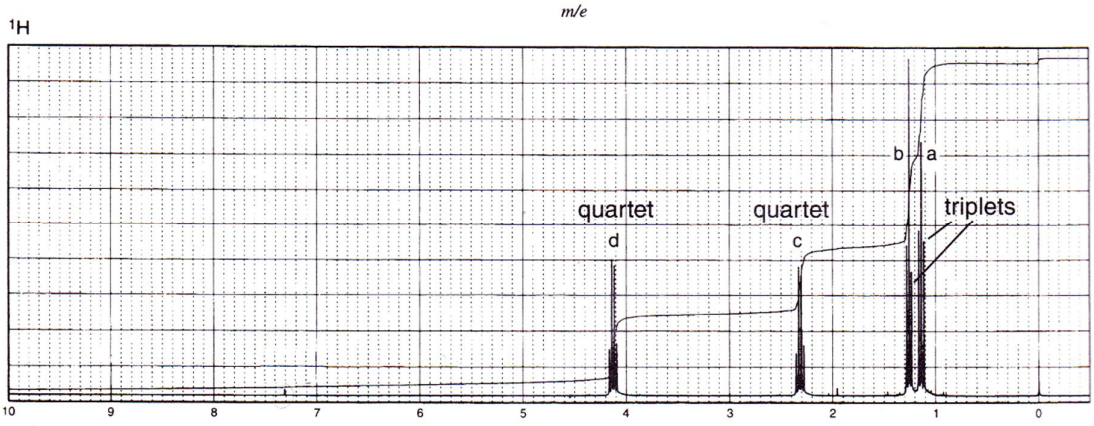
δ / ppm	No. of ^1H	Multiplicity	Deductions
2.1	3	s	-C**H$_3$** with no H on adj C Deshielded by electron-withdrawing ketone group
3.7	2	s	-C**H$_2$**- with no H on adj C Deshielded by ring current and electron-withdrawing ketone group
7.1 – 7.4	5	m	Aromatic H on mono-substituted phenyl ring

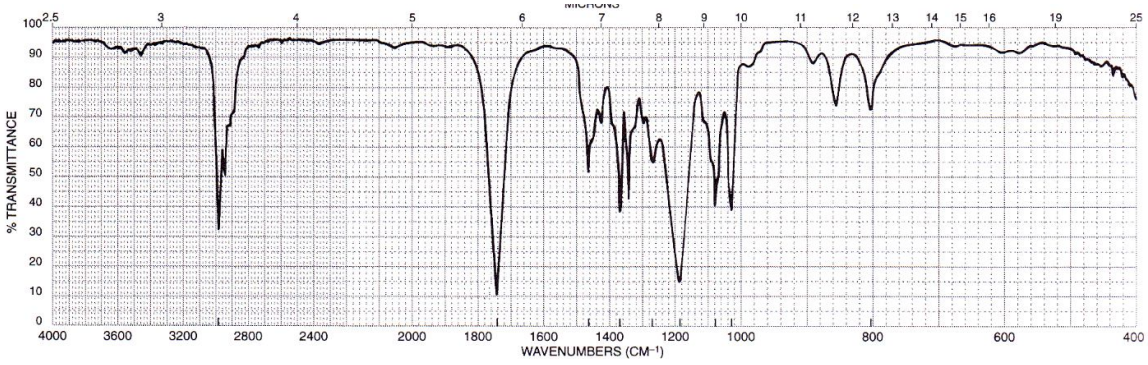
Structure:



3 Deduce the structure of compound **A**, giving your reasoning. [8]







IR

absorption	bond
1740	C=O
1200	C–O

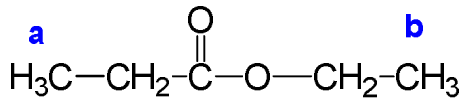
- **Absence of peak at 3230 to 3500 cm^{-1}** suggests **absence of O–H stretch** ⇒ **No alcohol**
- The **presence of a C–O** (strong and broad) **at 1200 cm^{-1}** and **C=O at 1740 cm^{-1}** confirm the identity of an **ester** functional group.

NMR

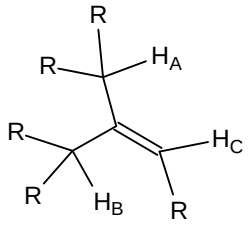
chemical shift /ppm	splitting pattern	No. of adjacent protons	relative peak area	group responsible
1.15	triplet	2	3	–C**H$_3$ (a)** adj to a -CH_2-
1.25	triplet	2	3	–C**H$_3$ (b)** adj to a -CH_2-
2.30	quartet	3	2	–C**H$_2$**CO– (adjacent to a –CO– and –CH_3)
4.15	quartet	3	2	–OC**H$_2$**– (adjacent to a –O– and –CH_3)

MS

m/e	species	
102	$(C_5H_{10}O_2)^+$	
57	$(CH_3CH_2CO)^+$	
29	$(CH_3CH_2)^+$	

A: 

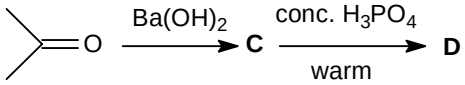
4 The ^{1}H NMR signals of protons on carbon atoms adjacent to C=C bonds can be split by protons at the far end of the C=C bond.



For example, protons H_A and H_C with split each other with a small coupling constant J_{AC}. Protons H_B and H_C will also split each other with coupling constant J_{BC}. J_{AC} and J_{BC} are often not equal.

Protons H_A and H_B may not be equivalent because of the restricted rotation around the C=C bond.

(a) Propanone undergoes the following sequence of reactions.



The infra-red and ^{1}H NMR spectra of compound **C** are shown in Fig. 2.1 and Fig. 2.2.

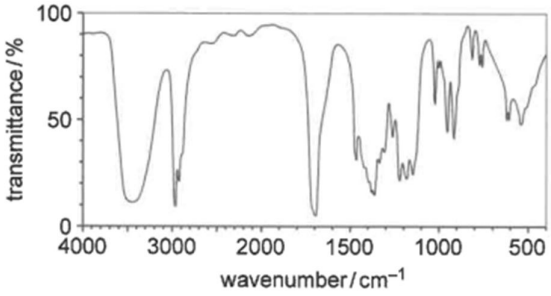


Fig. 2.1 The infra-red spectrum of compound **C**

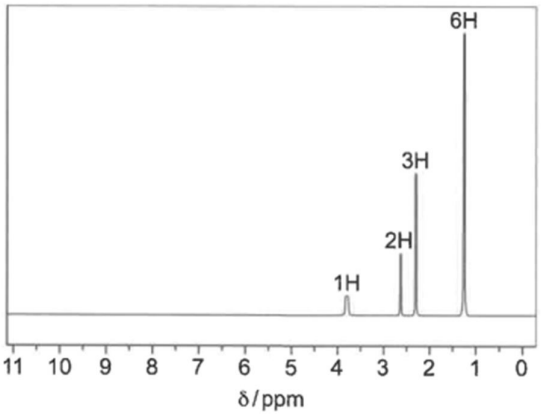


Fig. 2.2 The ^{1}H NMR spectrum of compound **C**

The mass spectrum of **C** shows major peaks at *m/z* values of 15, 43, 58, 101 and a small M^+ peak at *m/z* 116.

(i) Use this information to deduce the structure of **C**.
Explain your reasoning. [6]

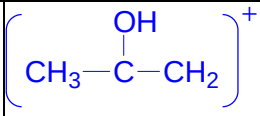
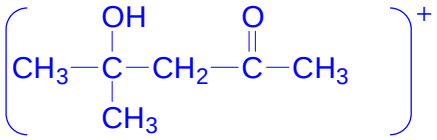
IR:

Wavenumber of absorbance / cm^{-1}	**Interpretation**
Strong absorption at 1700 cm^{-1}	C=O stretch in ketone
Strong absorption at 2800-3000 cm^{-1}	Aliphatic C–H stretch
Broad and strong peak at 3350 cm^{-1}	O–H bond stretch in alcohol

Presence of alcohol and ketone in **C**

C has a M_r of 116. Based on IR, it has two oxygen atoms (due to ketone and alcohol). Based on NMR, there are 12 hydrogen atoms.
Hence, no of C is (116 – 2x16 – 12x1)/12 = 6 and molecular formula is $C_6H_{12}O_2$.

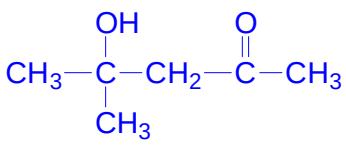
MS:

m/z	**Interpretation**
15	$[CH_3]^+$
43	$[CH_3CO]^+$
58	
101	116 – 101 = 15 Loss of CH_3 group. Hence m/z = 101 is $C_5H_9O_2$ $[CH_3COCH_2C(OH)CH_3]^+$ or $[COCH_2C(OH)(CH_3)_2]^+$
116	

NMR:

δ /ppm	**Multiplicity**	**No. of adjacent protons**	**No of H**	**Deduction**
1.5	Singlet	0	6	Two –C**H₃** adjacent to to C with no H
2.5	Singlet	0	3	–C**H₃** adjacent to C=O (no H on adjacent C)
2.7	Singlet	0	2	–C**H₂** adjacent to C=O (no H on adjacent C)
4.0	Singlet (broad)	0	1	Labile –O–H

Structure of **C**:



The infra-red and ^{1}H NMR spectra of compound **D** are shown in Fig. 2.3 and Fig. 2.4.

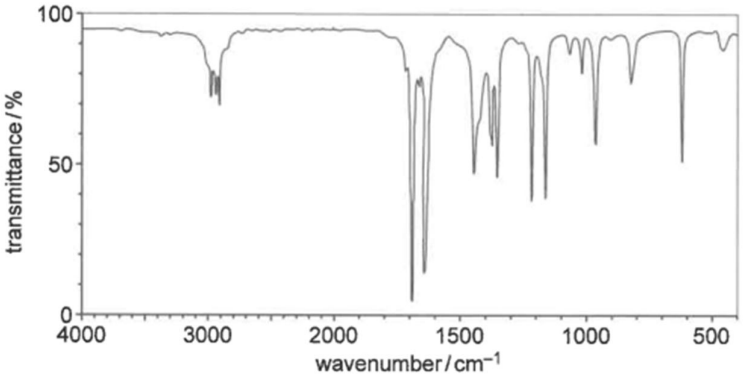


Fig. 2.3 The infra-red spectrum of compound **D**

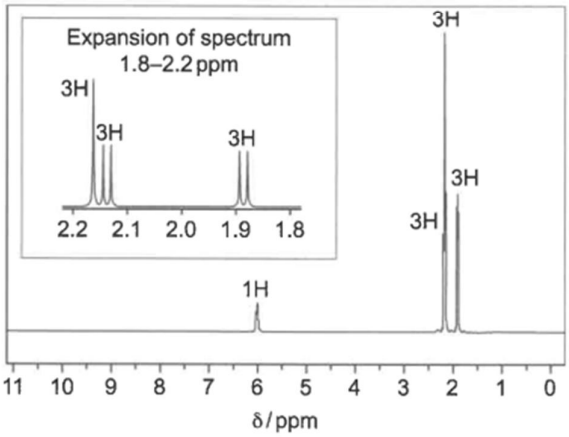


Fig. 2.4 The ^{1}H NMR spectrum of compound **D**

(ii) Use Fig. 2.3 and Fig. 2.4 to deduce the structure of **D**.
Explain your reasoning. [4]

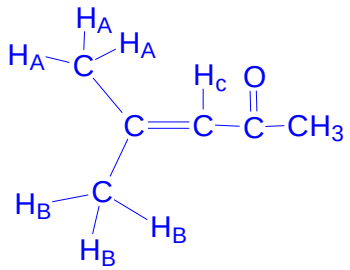
IR:

Wavenumber of absorbance / cm^{-1}	Interpretation
Strong absorption at 1700 cm^{-1}	C=O stretch in ketone
Weak absorption at 3000 cm^{-1}	Alkenes –C=H

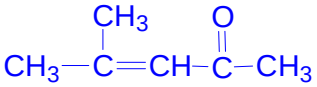
NMR:

δ /ppm	Multiplicity	No. of adjacent protons	No of H	Deduction
1.90	Doublet	1	3	–C**H₃** adjacent to C=C and split by the proton on the far end of C=C (H_A or H_B split by H_C)
2.11	Doublet	1	3	–C**H₃** adjacent to C=C and split by the proton on the far end of C=C (H_A or H_B split by H_C)
2.19	Singlet	0	3	–C**H₃** adjacent to C=O (no H on adjacent C)
6.0	Multiplet	6	1	=C**H** adjacent to $(CH_3)_2C$= and split by the protons on the two CH_3 (H_C split by H_A and H_B)

Note:

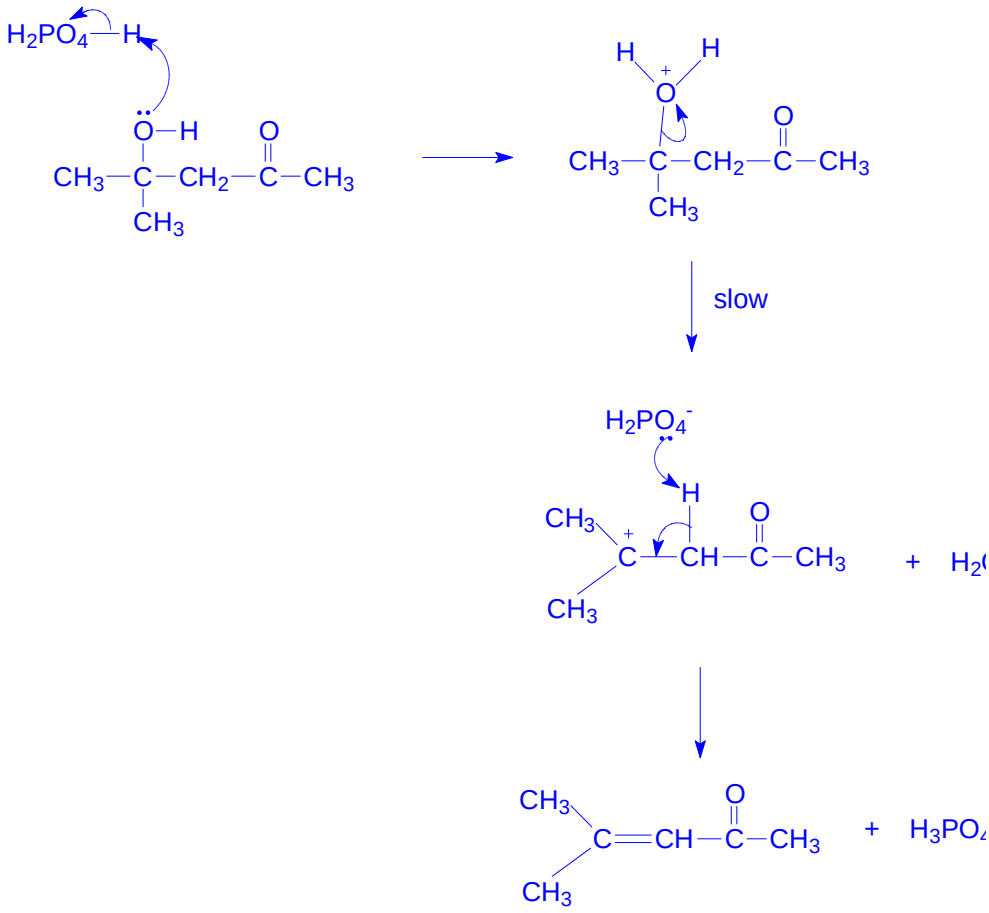


Structure of **D**:

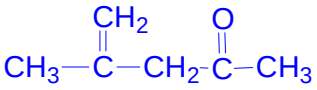


(iii) By considering the structure of compound **C**, suggest a mechanism for the reaction of **C** with warm conc. $H_3PO_4$to produce **D**, and label the rate-determining step. [3]

C is a tertiary alcohol, so it is likely to undergo E1.



(iv) The reaction of **C** with warm H_3PO_4 could produce two possible constitutional isomers.
Draw the structure of the other isomer, and suggest a reason why isomer **D** if formed, rather than the other isomer. [1]



D is more substituted and hence more stable.

(b) Another sequence of reactions starting with propanone is shown in Fig. 2.5.

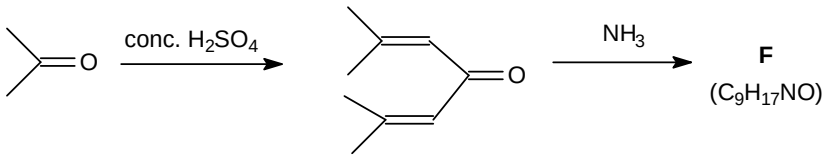


Table 2.1 lists the peak in the ^1H NMR spectrum of **F**.

Table 2.1

δ/ppm	splitting pattern	number of H atoms
1.04	singlet	12
2.33	singlet	4
2.70	broad singlet	1

The infra-red spectrum of **F** includes a strong peak at 1700 cm^{-1} and a weak peak at 3320 cm^{-1}.

Use the information given to suggest a structure for compound **F**.
Explain your reasoning. [4]

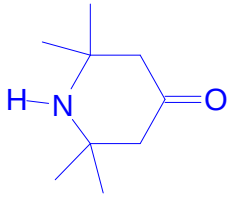
IR:

Wavenumber of absorbance / cm^{-1}	**Interpretation**
Strong peak at 1700 cm^{-1}	C=O stretch in ketone
Weak absorption at 3320 cm^{-1}	N–H in amines (since there is only one O)

NMR:

δ /ppm	**Multiplicity**	**No of H**	**Deduction**
1.04	Singlet	12	Four –C**H$_3$** with no H on adjacent C
2.33	Singlet	4	Two –C**H$_2$** no H on adjacent C and adjacent to C=O
2.70	Broad Singlet	1	–N–H in amines

Structure of **F**:



Note

E reacts with ammonia via nucleophilic addition. Ammonia can attack either at the carbonyl carbon atom or the electron-deficient disubstituted alkene C atom.

From the strong peak at 1700 cm^{-1} in the IR spectrum, there is a C=O group in **F**, hence the nucleophile attacks at the disubstituted alkene C atom. The weak peak at 3320 cm^{-1} corresponds to N-H stretch in the amine.

In the NMR spectrum, the broad singlet corresponds to 1 labile proton present in the amine N-H. From the relatively few number of signals and the even number of H atoms (except the broad singlet), compound **F** is likely to be symmetrical.

[Total:18]
2021 A Level H3 paper