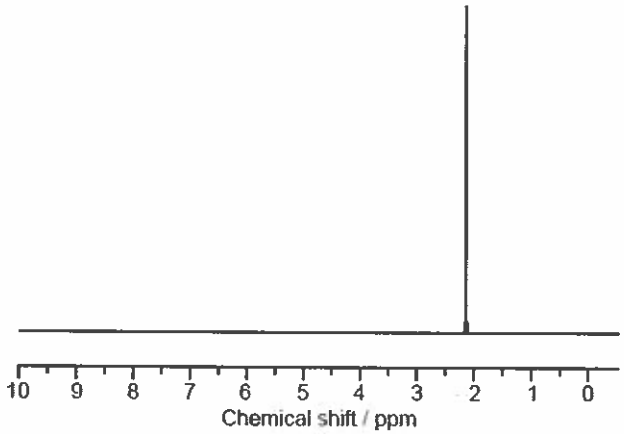
Practice Topic 11 questions *[55 marks]*

1. What can be deduced from the following ^{1}H NMR spectrum? *[1 mark]*



A. There is only one hydrogen atom in the molecule.

B. There is only one hydrogen environment in the molecule. only 1 peak

C. The molecule is a hydrocarbon.

D. There is only one isotope in the element.

Markscheme

B

Examiners report

[N/A]

2. What information is provided by ^{1}H NMR, MS and IR for an organic compound? *[1 mark]*

I. ^{1}H NMR: chemical environment(s) of protons
II. MS: fragmentation pattern
III. IR: types of functional group

A. I and II only

B. I and III only

C. II and III only

D. I, II and III

Markscheme

D

Examiners report

[N/A]

3. What can be determined about a molecule from the number of signals in its ^{1}H NMR spectrum? *[1 mark]*

A. Bonds present

B. Molecular formula

C. Molecular mass

D. Number of hydrogen environments

Markscheme

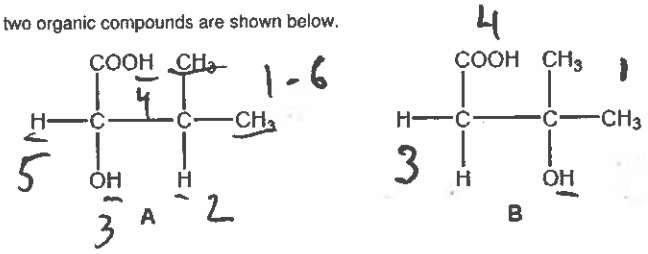
D

Examiners report

[N/A]

The reactivity of organic compounds depends on the nature and positions of their functional groups.

The structural formulas of two organic compounds are shown below.



4a. Deduce the type of chemical reaction and the reagents used to distinguish between these compounds. *[1 mark]*

Oxidization by $K_2Cr_2O_7$ or K_2MnO_4

Markscheme

oxidation/redox AND acidified «potassium» dichromate(VI)

OR

oxidation/redox AND «acidified potassium» manganate(VII)

Accept "acidified «potassium» dichromate" OR "«acidified potassium» permanganate".

Accept name or formula of the reagent(s).

Examiners report

[N/A]

4b. State the observation expected for each reaction giving your reasons. *[2 marks]*

Compound **A**: orange → green

2nd ary hydroxyl

Compound **B**: no chang (tertiary OH)

Markscheme

ALTERNATIVE 1 using $K_2Cr_2O_7$:

Compound A: orange to green ***AND*** secondary hydroxyl

OR

Compound A: orange to green ***AND*** hydroxyl oxidized «by chromium(VI) ions»

Compound B: no change ***AND*** tertiary hydroxyl «not oxidized by chromium(VI) ions»

*Award [1] for "A: orange to green **AND** B: no change".*

*Award [1] for "A: secondary hydroxyl **AND** B: tertiary hydroxyl".*

ALTERNATIVE 2 using $KMnO_4$:

Compound A: purple to colourless ***AND*** secondary hydroxyl

OR

Compound A: purple to colourless ***AND*** hydroxyl oxidized «by manganese(VII) ions»

Compound B: no change ***AND*** tertiary hydroxyl «not oxidized by manganese(VII) ions»

Accept "alcohol" for "hydroxyl".

*Award [1] for "A: purple to colourless **AND** B: no change"*

*Award [1] for "A: secondary hydroxyl **AND** B: tertiary hydroxyl".*

Accept "purple to brown" for A.

Examiners report

[N/A]

4c. Deduce the number of **signals** and the ratio of areas under the signals in the ^1H NMR spectra of the two compounds. *[4 marks]*

Compound	Number of signals	Ratio of areas
A	5	6 : 1 : 1 : 1 : 1
B	4	6 : 1 : 2 : 1

Markscheme

Compound	Number of signals	Ratio of areas
A	5 ✓	6:1:1:1:1 ✓
B	4 ✓	6:1:1:2 ✓

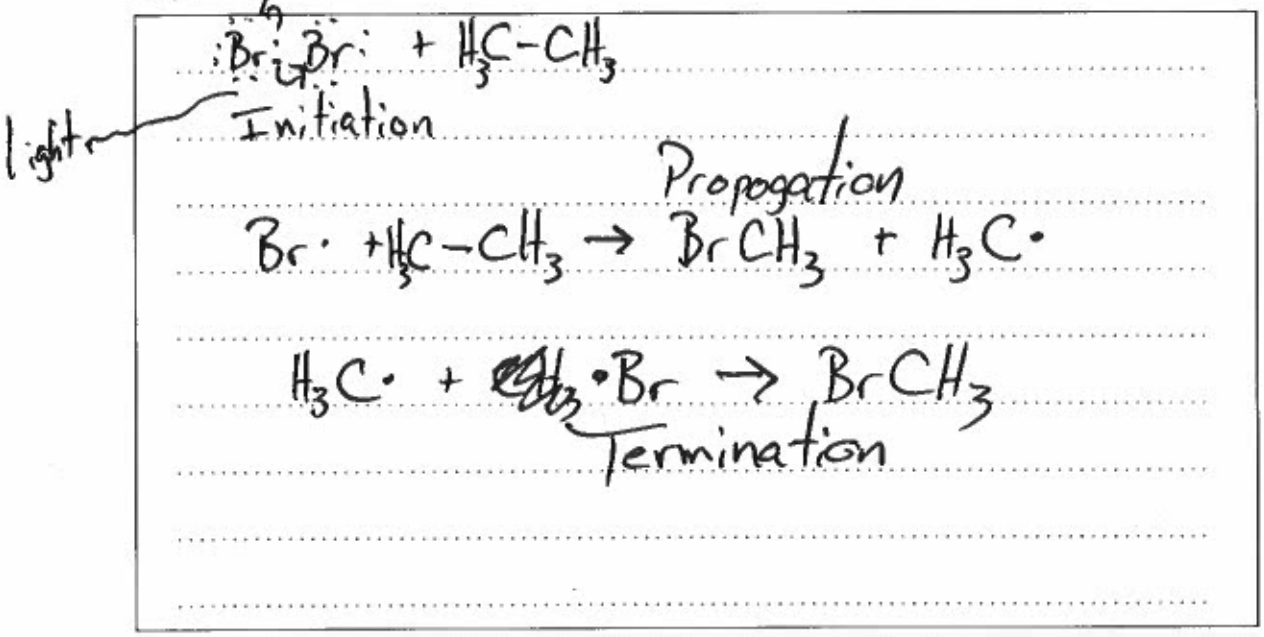
Accept ratio of areas in any order.

Do not apply ECF for ratios.

Examiners report

[N/A]

4d. Explain, with the help of equations, the mechanism of the free-radical substitution reaction of ethane with bromine in presence of sunlight. *[4 marks]*



Markscheme

Initiation:

$Br_2 \xrightarrow{UV\ /hv/heat} 2Br^{\bullet}$

Propagation:

$Br^{\bullet} + C_2H_6 \rightarrow C_2H_5^{\bullet} + HBr$

$C_2H_5^{\bullet} + Br_2 \rightarrow C_2H_5Br + Br^{\bullet}$

Termination:

$Br^{\bullet} + Br^{\bullet} \rightarrow Br_2$

OR

$C_2H_5^{\bullet} + Br^{\bullet} \rightarrow C_2H_5Br$

OR

$C_2H_5^{\bullet} + C_2H_5^{\bullet} \rightarrow C_4H_{10}$

Reference to UV/hv/heat not required.

Accept representation of radical without • (eg. Br, C_2H_5) if consistent throughout mechanism.

Accept further bromination.

*Award **[3 max]** if initiation, propagation and termination are not stated or are incorrectly labelled for equations.*

*Award **[3 max]** if methane is used instead of ethane, and/or chlorine is used instead of bromine.*

Examiners report

[N/A]

This question is about carbon and chlorine compounds.

5a. Ethane, C_2H_6, reacts with chlorine in sunlight. State the type of this reaction and the name of the mechanism by which it occurs. *[1 mark]*

Type of reaction: substitution

Mechanism: free radical

Markscheme

substitution ***AND*** «free-»radical
OR
substitution ***AND*** chain

Award [1] for "«free-»radical substitution" or "S_R" written anywhere in the answer.

[1 mark]

Examiners report

[N/A]

5b. Formulate equations for the two propagation steps and one termination step in the formation of chloroethane from ethane. *[3 marks]*

Two propagation steps:

$Cl\cdot + H_3C-CH_3 \rightarrow ClCH_3 + \cdot CH_3$

$C_2H_5\cdot + Cl_2 \rightarrow C_2H_5Cl + Cl\cdot$

One termination step: $Cl\cdot + \cdot C_2H_5 \rightarrow C_2H_5Cl$

C

Markscheme

Two propagation steps:

$C_2H_6 + \cdot Cl \rightarrow C_2H_5\cdot + HCl$

$C_2H_5\cdot + Cl_2 \rightarrow C_2H_5Cl + \cdot Cl$

One termination step:

$C_2H_5\cdot + C_2H_5\cdot \rightarrow C_4H_{10}$

OR

$C_2H_5\cdot + \cdot Cl \rightarrow C_2H_5Cl$

OR

$\cdot Cl + \cdot Cl \rightarrow Cl_2$

Accept radical without · if consistent throughout.

Allow ECF from incorrect radicals produced in propagation step for M3.

[3 marks]

Examiners report

[N/A]

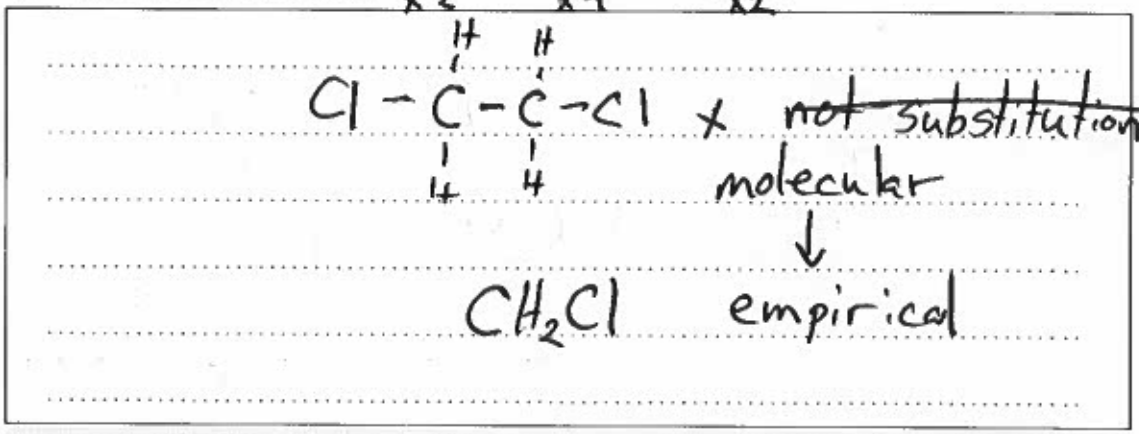
~~Alkane + Halogen → elimination~~ X

5c. One possible product, X, of the reaction of ethane with chlorine has the following composition by mass: *[2 marks]*

carbon: 24.27%, hydrogen: 4.08%, chlorine: 71.65%

Determine the empirical formula of the product.

12.01 ×2 | 1.01 ×4 | 34.45 ×2



Markscheme

$C = \frac{24.27}{12.01} = 2.021$ ***AND*** $H = \frac{4.08}{1.01} = 4.04$ ***AND*** $Cl = \frac{71.65}{35.45} = 2.021$

«hence» CH_2Cl

Accept
$\frac{24.27}{12.01} : \frac{4.08}{1.01} : \frac{71.65}{35.45}$.

*Do **not** accept $C_2H_4Cl_2$.*

Award [2] for correct final answer.

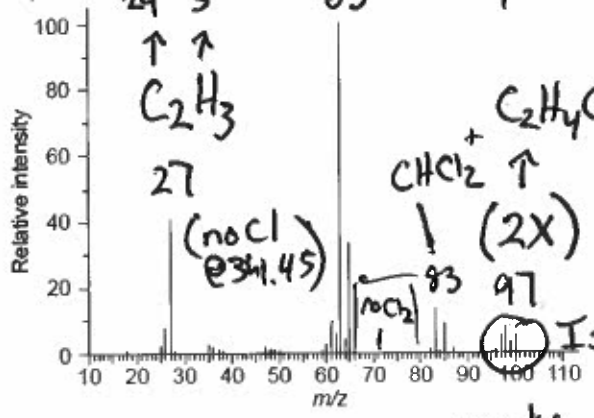
[2 marks]

Examiners report

[N/A]

5d. The mass and ^{1}H NMR spectra of product **X** are shown below. Deduce, giving your reasons, its structural formula and hence the name of the compound. *[3 marks]*

Mass spectrum:



24 3
↑ ↑
C_2H_3
27

63 C_2H_4Cl

CH_2Cl

$C_2H_4Cl_2^+$

$CHCl_2^+$
↑
(2X)
83 97

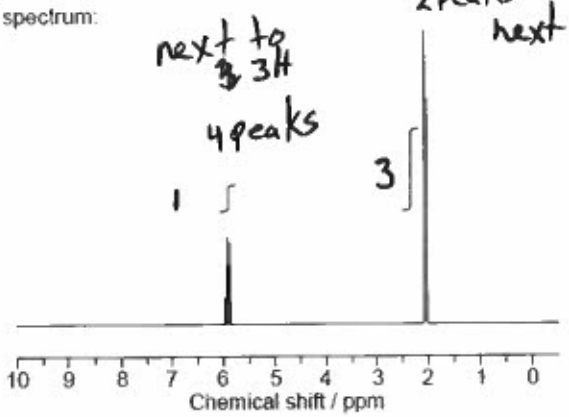
(no Cl @34.45)

CH_2Cl

Cl → 34.45
C → 12.01
H_2 → 2.02
48.48 (not present)

Isotopes
x2 = 97.6

^{1}H NMR spectrum:



(H+1 rule)

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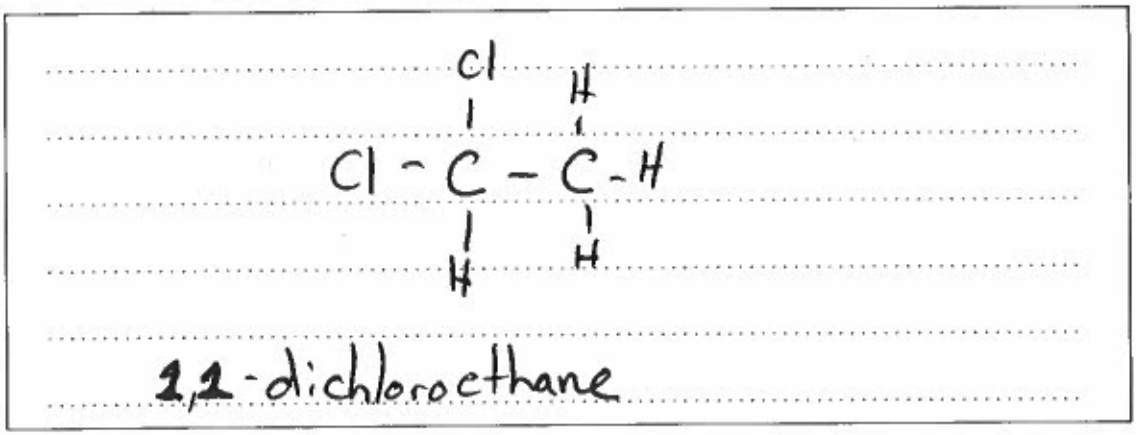


Markscheme

molecular ion peak(s) «about» *m/z* 100 ***AND*** «so» $C_2H_4Cl_2$ «isotopes of Cl»

two signals «in ^{1}H NMR spectrum» ***AND*** «so» CH_3CHCl_2
OR
«signals in» 3:1 ratio «in ^{1}H NMR spectrum» ***AND*** «so» CH_3CHCl_2
OR
one doublet and one quartet «in 1H NMR spectrum» ***AND*** «so» CH_3CHCl_2

1,1-dichloroethane

Accept "peaks" for "signals".

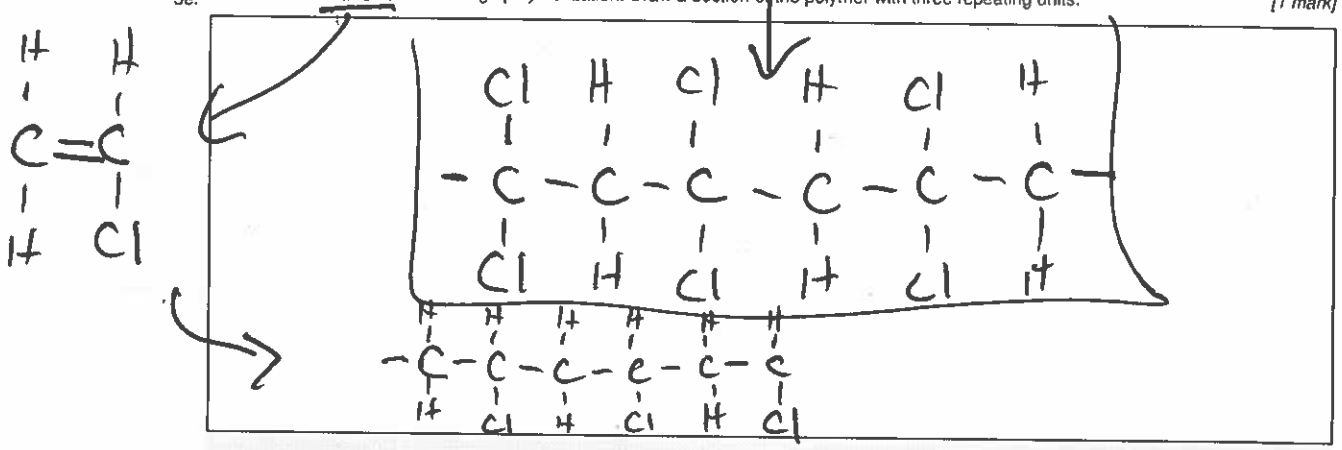
Allow ECF for a correct name for M3 if an incorrect chlorohydrocarbon is identified

[3 marks]

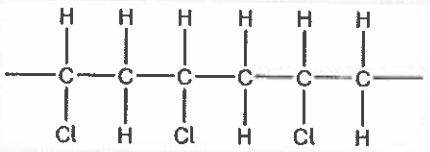
Examiners report

[N/A]

5e. Chloroethene, C_2H_3Cl, can undergo polymerization. Draw a section of the polymer with three repeating units. *[1 mark]*

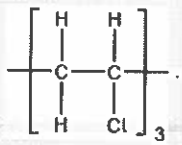


Markscheme



Continuation bonds must be shown.

Ignore square brackets and "n".

Accept  .

Accept other versions of the polymer, such as head to head and head to tail.

Accept condensed structure provided all C to C bonds are shown (as single).

[1 mark]

Examiners report

[N/A]

This question is about carbon and chlorine compounds.

6a. Ethane, C_2H_6, reacts with chlorine in sunlight. State the type of this reaction and the name of the mechanism by which it occurs. *[1 mark]*

Type of reaction: Substitution

Mechanism: Free radical

Markscheme

substitution ***AND*** «free-»radical

OR

substitution ***AND*** chain

Award [1] for "«free-»radical substitution" or "Sn" written anywhere in the answer.

[1 mark]

Examiners report

[N/A]

6b. Formulate equations for the two propagation steps and one termination step in the formation of chloroethane from ethane. *[3 marks]*

Two propagation steps:

.....

.....

.....

.....

One termination step:

.....

.....

Sameas 5

.....

.....

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.....

.....

Markscheme

Two propagation steps:

$C_2H_6 + \bullet Cl \rightarrow C_2H_5\bullet + HCl$

$C_2H_5\bullet + Cl_2 \rightarrow C_2H_5Cl + \bullet Cl$

One termination step:

$C_2H_5\bullet + C_2H_5\bullet \rightarrow C_4H_{10}$

OR

$C_2H_5\bullet + \bullet Cl \rightarrow C_2H_5Cl$

OR

$\bullet Cl + \bullet Cl \rightarrow Cl_2$

Accept radical without • if consistent throughout.

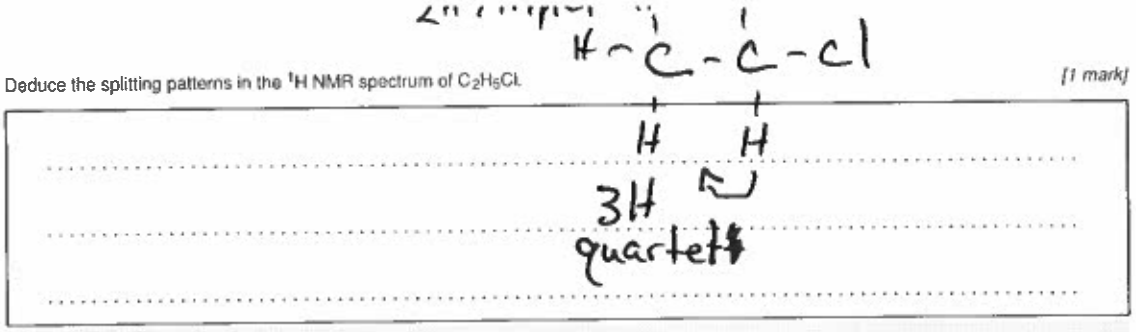
Allow ECF for incorrect radicals produced in propagation step for M3.

[3 marks]

Examiners report

[N/A]

6c. Deduce the splitting patterns in the ^{1}H NMR spectrum of C_2H_5Cl. *[1 mark]*



Markscheme

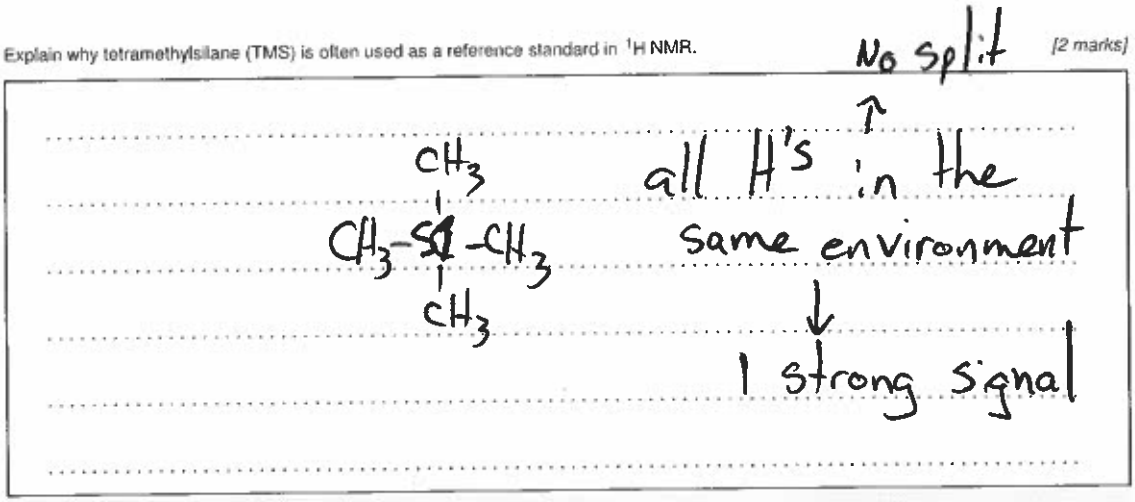
triplet ***AND*** quartet

[1 mark]

Examiners report

[N/A]

6d. Explain why tetramethylsilane (TMS) is often used as a reference standard in ^{1}H NMR. *[2 marks]*



Markscheme

chemical shift/signal outside range of common chemical shift/signal

strong signal/12/all H atoms in same environment

OR

singlet/no splitting of the signal

volatile/easily separated/easily removed

OR

inert/stabl

contains three common NMR nuclei/^{1}H and ^{13}C and ^{29}Si

Do not accept chemical shift = 0.

[2 marks]

Examiners report

[N/A]

6e. One possible product, **X**, of the reaction of ethane with chlorine has the following composition by mass: *[2 marks]*

carbon: 24.27%, hydrogen: 4.08%, chlorine: 71.65%

Determine the empirical formula of the product. 2C 4H 2Cl

CH_2Cl

Markscheme

$\mathrm{C} = \frac{24.27}{12.01} = 2.021$ ***AND*** $\mathrm{H} = \frac{4.08}{1.01} = 4.04$ ***AND*** $\mathrm{Cl} = \frac{71.65}{35.45} = 2.021$

«hence» CH_2Cl

Accept

$\frac{24.27}{12.01}$;

$\frac{4.08}{1.01}$;

$\frac{71.65}{35.45}$;

*Do **not** accept $C_2H_4Cl_2$.*

Award [2] for correct final answer.

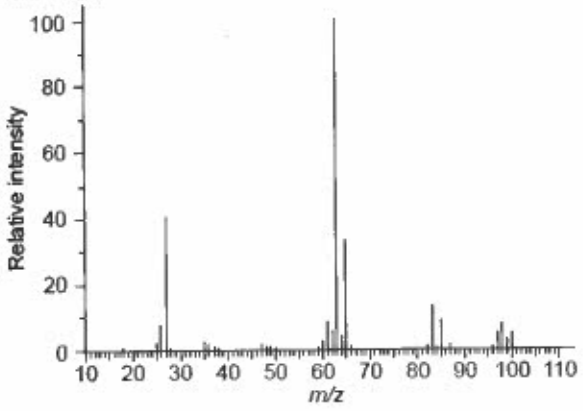
[2 marks]

Examiners report

[N/A]

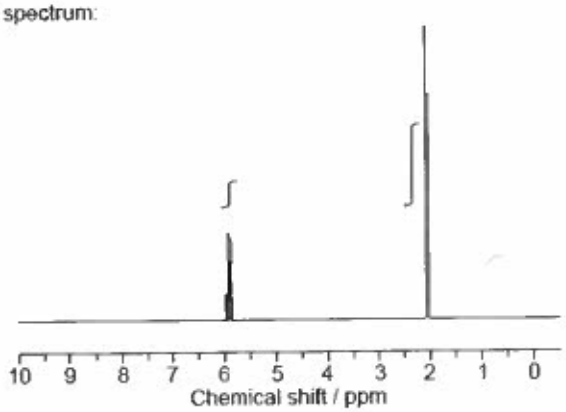
6f. The mass and ^{1}H NMR spectra of product **X** are shown below. Deduce, giving your reasons, its structural formula and hence the name of the compound. *[3 marks]*

Mass spectrum:



same

^{1}H NMR spectrum:



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Markscheme

molecular ion peak(s) «about» *m/z* 100 ***AND*** «so» $C_2H_4Cl_2$ «isotopes of Cl»

two signals «in ^{1}H NMR spectrum» ***AND*** «so» CH_3CHCl_2
OR
«signals in» 3:1 ratio «in ^{1}H NMR spectrum» ***AND*** «so» CH_3CHCl_2
OR
one doublet and one quartet «in ^{1}H NMR spectrum» ***AND*** «so» CH_3CHCl_2

1,1-dichloroethane

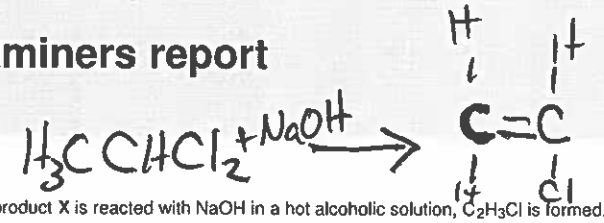
Accept "peaks" for "signals".

Allow ECF for a correct name for M3 if an incorrect chlorohydrocarbon is identified.

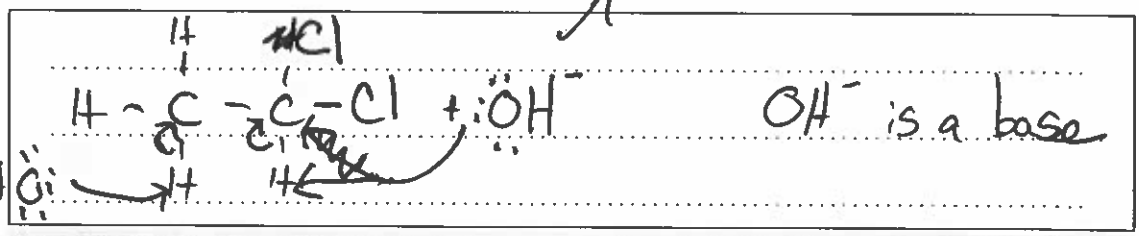
[3 marks]

Examiners report

[N/A]



6g. When the product **X** is reacted with NaOH in a hot alcoholic solution, C_2H_3Cl is formed. State the role of the reactant NaOH other than as a nucleophile. *[1 mark]*



Markscheme

base
OR
proton-acceptor

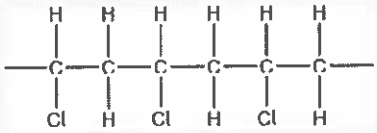
[1 mark]

Examiners report

[N/A]

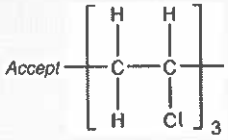
6h. Chloroethene, C_2H_3Cl, can undergo polymerization. Draw a section of the polymer with three repeating units. *[1 mark]*

Markscheme



Continuation bonds must be shown.

Ignore square brackets and "n".

Accept  .

Accept other versions of the polymer, such as head to head and head to tail.

Accept condensed structure provided all C to C bonds are shown (as single).

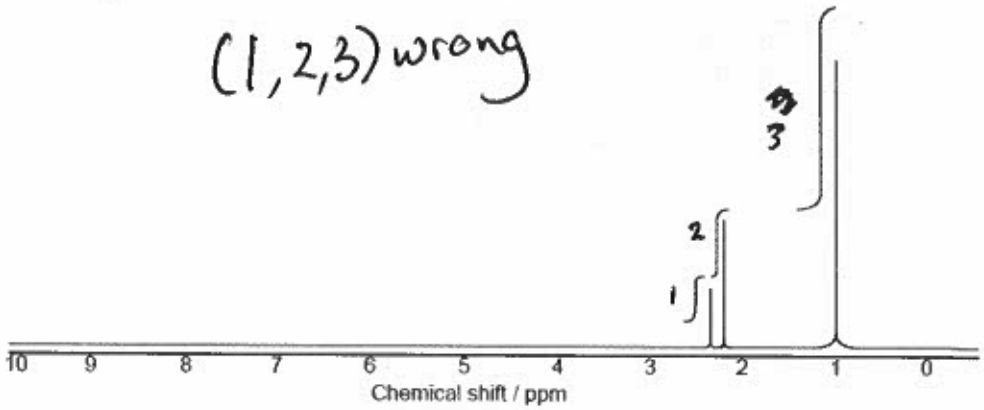
[1 mark]

Examiners report

[N/A]

A compound with a molecular formula $C_7H_{14}O$ produced the following high resolution ^1H NMR spectrum.

(1,2,3) wrong



7a. Deduce what information can be obtained from the ^1H NMR spectrum. *[3 marks]*

Number of hydrogen environments: 3

Ratio of hydrogen environments: ~~1:2:3~~ 2:3:9 Should be given?

Splitting patterns: All singlets

Markscheme

Number of hydrogen environments: 3

Ratio of hydrogen environments: 2:3:9

Splitting patterns: «all» singlets

Accept any equivalent ratios such as 9:3:2.

Accept "no splitting".

[3 marks]

Examiners report

[N/A]

IK

7b. Identify the functional group that shows stretching at 1710 cm^{-1} in the infrared spectrum of this compound using section 26 of the data booklet and the ^1H NMR. *[1 mark]*

? why? HNMR

C=O

Markscheme

carbonyl
OR
C=O

Accept "ketone" but not "aldehyde".

[1 mark]

(from HNMR)
Why ... ; if aldehyde only 2 H environments

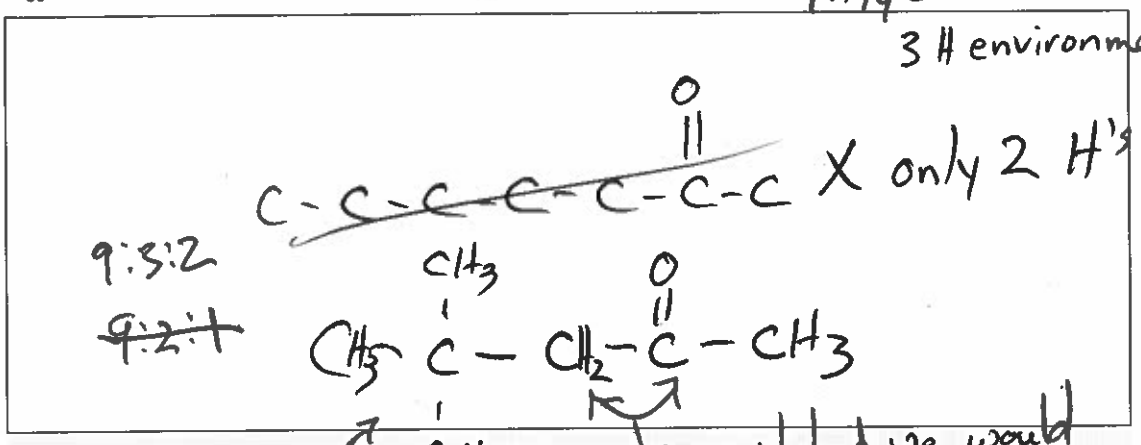
Examiners report

[N/A]

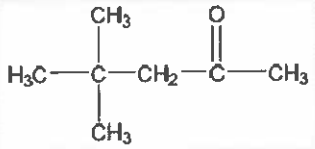
7c. Suggest the structural formula of this compound. *[2 marks]*

Remember $C_7H_{14}O$

3 H environments



Markscheme



Accept $(CH_3)_3CCH_2COCH_3$.

Award [1] for any aldehyde or ketone with $C_7H_{14}O$ structural formula.

[2 marks]

Examiners report

[N/A]

Br_2 C_6H_{14} C_6H_{12} C_6H_6

7d. Bromine was added to hexane, hex-1-ene and benzene. Identify the compound(s) which will react with bromine in a well-lit laboratory. *[1 mark]*

$Br_2 + C_6H_{14} \rightarrow$ Free Radical substitution

$Br_2 + C_6H_{12} \rightarrow$ Addition

$Br_2 + C_6H_6 \rightarrow$ No reaction (Resonance Stabilization)

Markscheme

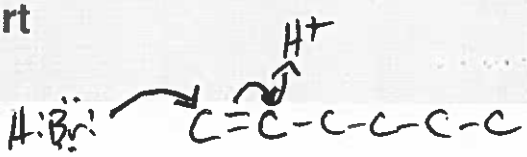
hexane ***AND*** hex-1-ene

*Accept "benzene **AND** hexane **AND** hex-1-ene".*

[1 mark]

Examiners report

[N/A]



7e. Deduce the structural formula of the main organic product when hex-1-ene reacts with hydrogen bromide. *[1 mark]*

HBr not structural

$Br_2 + C_6H_{12} \rightarrow C_6H_{13}Br \rightarrow CH_2BrCH_2CH_2CH_2CH_2CH_3$

$C_6H_{12}Br_2$ X

Markscheme

$CH_3CH_2CH_2CH_2CHBrCH_3$

Accept displayed formula but not molecular formula.

[1 mark]

Examiners report

[N/A]

7f. State the reagents and the name of the mechanism for the nitration of benzene. *[2 marks]*

Reagents:

.....

Name of mechanism:

.....

HL only

.....

.....

.....

Markscheme

Reagents: «concentrated» sulfuric acid ***AND*** «concentrated» nitric acid

Name of mechanism: electrophilic substitution

[2 marks]

Examiners report

[N/A]

7g. Outline, in terms of the bonding present, why the reaction conditions of halogenation are different for alkanes and benzene. *[1 mark]*

HL

.....

.....

.....

Markscheme

benzene has «delocalized» π bonds «that are susceptible to electrophile attack» ***AND*** alkanes do not

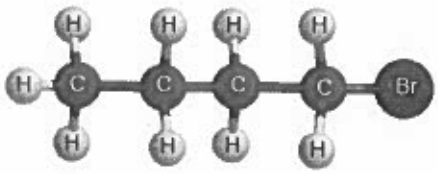
*Do **not** accept "benzene has single and double bonds".*

[1 mark]

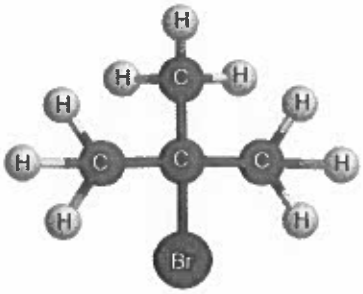
Examiners report

[N/A]

7h. Below are two isomers, A and B, with the molecular formula C_4H_9Br. *[3 marks]*



A

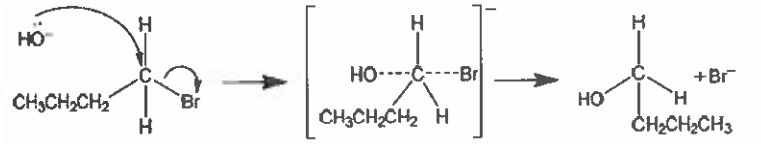


B

HL

Explain the mechanism of the nucleophilic substitution reaction with NaOH(aq) for the isomer that reacts almost exclusively by an S_N2 mechanism using curly arrows to represent the movement of electron pairs.

Markscheme



curly arrow going from lone pair/negative charge on O in ^-OH to C

curly arrow showing Br leaving

representation of transition state showing negative charge, square brackets and partial bonds

HL

Accept OH^- with or without the lone pair.

Do not allow curly arrows originating on H in OH^-.

Accept curly arrows in the transition state.

Do not penalize if HO and Br are not at 180°.

Do not award M3 if OH–C bond is represented.

*Award **[2 max]** if wrong isomer is used.*

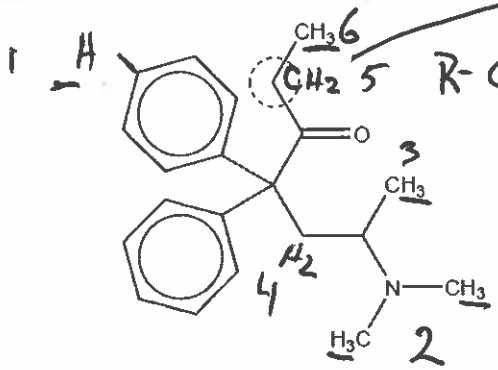
[3 marks]

Examiners report

[N/A]

The structures of morphine, diamorphine and codeine are given in section 37 of the data booklet.

Methadone is used to treat heroin addiction. ^1H NMR spectroscopy can be used to study its structure.



Next to CH3 : O=C

R-CH2-R ~ 1.5 x

R-CH2-C(=O)-R

2.2-2.7

8a. Predict the number of different hydrogen environments in the molecule ignoring the benzene rings. *[1 mark]*

6

Markscheme

6

[1 mark]

Examiners report

[N/A]

8b. Predict the chemical shift and the splitting pattern seen for the hydrogens on the carbon atom circled in the diagram. Use section 27 *[2 marks]* of the data booklet.

Chemical shift: 2.2-2.7 → R-CH_2-C(=O)-R

Splitting pattern: Next to CH_3 → Quartet

Markscheme

Chemical shift:
2.2–2.7 «ppm»

Splitting pattern:
quartet/q

[2 marks]

Examiners report

[N/A]