ASSESSMENT and QUALIFICATIONS ALLIANCE

General Certificate if Education

Chemistry 5421

CHM3/W Introduction to Organic Chemistry

Mark Scheme

2006 examination – January series

Mark schemes are prepared by the Principal Examiner and considered, together with the relevant questions, by a panel of subject teachers. This mark scheme includes any amendments made at the standardisation meeting attended by all examiners and is the scheme which was used by them in this examination. The standardisation meeting ensures that the mark scheme covers the candidates' responses to questions and that every examiner understands and applies it in the same correct way. As preparation for the standardisation meeting each examiner analyses a number of candidates' scripts: alternative answers not already covered by the mark scheme are discussed at the meeting and legislated for. If, after this meeting, examiners encounter unusual answers which have not been discussed at the meeting they are required to refer these to the Principal Examiner.

It must be stressed that a mark scheme is a working document, in many cases further developed and expanded on the basis of candidates' reactions to a particular paper. Assumptions about future mark schemes on the basis of one year's document should be avoided; whilst the guiding principles of assessment remain constant, details will change, depending on the content of a particular examination paper.

CHM3/W Introduction to Organic Chemistry

SECTION A

Question 1

(a) (i) any two from:
show a gradation/trend/gradual change in physical properties/ a specified property
differ by CH_2
chemically similar or react in the same way
have the same functional group 2
(penalise "same molecular formula")
(penalise "same empirical formula")

(ii) fractional distillation or fractionation 1

(iii) contains only single bonds or has no double bonds 1
(*credit "every carbon is bonded to four other atoms", provided it does not contradict by suggesting that this will always be H*)

(b) (i) the molecular formula gives the actual number of atoms of each element/type in a molecule/hydrocarbon/compound/formula 1
(penalise "amount of atoms")
(penalise "ratio of atoms")

(ii) $C_{14}H_{30}$ only 1
(penalise as a contradiction if correct answer is accompanied by other structural formulae)

(iii) $C_{10}H_{22} + 5½O_2 \longrightarrow 10C + 11H_2O$ 1
(or double this equation)

(c) (i) $½N_2 + ½O_2 \longrightarrow NO$ 1
(or double this equation)

(ii) Platinum or palladium or rhodium 1

(iii) $2CO + 2NO \longrightarrow 2CO_2 + N_2$ or

$2NO \longrightarrow N_2 + O_2$ or
(ignore extra O2 molecules provided the equation balances)

$C + 2NO \longrightarrow CO_2 + N_2$
(or half of each of these equations)

$C_8H_{18} + 25NO \longrightarrow 8CO_2 + 12½N_2 + 9H_2O$ 1
(or double this equation)

Total 10

Question 2

(a) Ag or silver or silver-based or silver on an alumina base 1
(penalise specific silver compounds)

epoxyethane 1

(b) electrophilic addition 1

M1: curly arrow <u>from C=C bond</u> towards/alongside the side of H atom on $H^{-}OSO_2OH$ 1
(penalise M1 if arrow to H_2SO_4 OR to formal charge on H of $H^{-}O$ bond)
(ignore partial charges on H and O of H_2SO4, but penalise if these are incorrect on the H atom being attacked)
(credit M1 and M2 if correct curly arrow to H+ provided the anion is present)

M2: curly arrow from <u>H-O bond</u> towards/alongside the side of the O atom on $H\text{-}OSO_2OH$ 1
(credit the arrow even if there are partial or formal charges on H and O, but the structure of H_2SO_4 is correct)

M3: correct structure of the carbocation 1
(penalise use of 'sticks' in this structure)
M4: curly arrow <u>from lone pair on an individual oxygen atom</u> of (correct formula for) hydrogensulphate ion towards/alongside C atom bearing the positive charge 1
(insist that the an ion has the correct formula with a lone pair of electrons and a negative charge)

(c) (i) ethanal 1
correct structure for ethanal 1
(aldehyde functional group must be drawn out)

(ii) oxidation or redox 1

Total 10

Question 3

(a) (i) (free-) radical substitution 1
(both words required for the mark)
initiation $Cl_2 \longrightarrow 2Cl\cdot$ 1
(credit correct half arrows, but penalise double headed arrows)

first propagation $CH_3Cl + Cl\cdot \longrightarrow \cdot CH_2Cl + HCl$ 1
second propagation $\cdot CH_2Cl + Cl_2 \longrightarrow CH_2Cl_2 + Cl\cdot$ 1
(penalise the absence of dots on radicals once only)
(penalise radical dot on Cl of CH_2Cl once only)

(ii) $CH_3Cl + Cl_2 \longrightarrow CH_2Cl_2 + HCl$ 1
(penalise if any radicals appear in this equation)

(b) M1: mol C = 10.1/12.0 and mol Cl = 89.9/35.5 1

M2: Ratio 0.842 : 2.53 OR 1 : 3 OR CCl3 1

M3: 237.0/Mr of CCl_3 = 237.0/118.5 = 2 Therefore C_2Cl_6 1
(correct answer gains full credit)

OR

M1: 237.0 x 10.1/100 and 237 x 89.9/100 1

M2: Ratio 23.9/12.0 : 213/35.5 *OR* 2 : 6 1

M3: C_2Cl_6 1
(correct answer gains full credit)

(c) any two from $CHBr_3$ or CBr_4 or $C_2H_2Br_4$ (or $CHBr_2CHBr_2$) or C_2Br_6 (or CBr_3CBr_3) 2
(ignore HBr or H_2)
(ignore equations and ignore names when given in addition to formulae)
(penalise names alone)

Total 10

Question 4

(a) 1(-)bromobutane 1

correct structure for 1-bromo-2-methylpropane 1
(C-C bonds must be clear where drawn)

(b) (base) elimination 1
(penalise other words before "elimination" e.g. nucleophilic)

M1: curly arrow from lone pair of electrons on oxygen of hydroxide ion 1
(insist on a lone pair of electrons on the oxygen atom and a negative charge, but only credit this mark if the attack is to a correct H atom) 1

M2: curly arrow from the middle of the C-H bond to the middle of the C-C bond 1
(only credit this mark if the arrow originates from the correct C-H bond and if an attempt has been made at M1)

M3: curly arrow from the middle of the C-Br bond towards/alongside the Br atom 1
(credit M3 independently unless the bond breaking is contradicted by an additional arrow)
(penalise curly arrow if the C-Br has a formal positive charge)
(credit full marks for an E1 mechanism, with M2 awarded for a correct curly arrow on the correct carbocation)
(award a maximum of two marks for either an incorrect haloalkane or an incorrect organic product)
(maximum 2 marks for use of 'sticks' for the haloalkane, unless RE from 2(b), when credit can be given)

(c) (i) M1: compounds with the same structural formula 1

M2: but the bonds/groups/atoms have different spatial arrangements or orientation or configuration/are arranged differently in space/3D 1
(ignore reference to the same molecular formula for M1)

(ii) M1: correct structural representation for cis-but-2-ene and its name or its identification as the cis isomer 1

M2: correct structural representation for trans-but-2-ene and its name or its identification as the trans isomer 1
(accept representations which are 90^{o} to linear)
(award one mark for two correct structures but either wrong/no names)
(maximum 1 mark for an incorrect alkene)

(iii) geometric(al) or cis-trans 1

(d) nucleophile or electron pair donor 1
(penalise "base")

(e) $CH_3CH_2CH_2CH_2Br + 2NH_3 \longrightarrow CH_3CH_2CH_2CH_2NH_2 + NH_4Br$ 2
(M1 correct product)
(M2 balanced equation using $2NH_3$ and leading to NH_4Br)
(penalise M1 for use of $C_4H_9NH_2$ or for incorrect haloalkane, but allow consequent correct balancing of equation with 2 moles of ammonia)

(1-)butylamine 1
(credit 1-aminobutane and butyl-1-amine)
(award QoL mark for correct spelling)

Total 15

Question 5

(a) M1: aqueous or solution in water or (aq) in the equation 1

M2: yeast or zymase 1
(do not credit "an enzyme", unless qualified)

M3: anaerobic/absence of oxygen/absence of air or neutral pH/pH value 6 – 8 1

M4 T in the range 30 – 40°C only 1
(ignore references to pressure)
(ignore uv light)

M5: fermentation 1

M6: $C_6H_{12}O_6 \longrightarrow 2CH_3CH_2OH + 2CO_2$ 1
(ignore state symbols but penalise M1 if the state symbol in the equation contradicts)

M7: $CH_3CH_2OH + 3O_2 \longrightarrow 2CO_2 + 3H_2O$ 1
(credit use of C_2H_5OH)
(penalise use of C_2H_6O once only in M6 or M7)

(b) M1: dehydration is the elimination of water or removal of combined water or qualified loss of/removal of water e.g. from a compound/molecule/alcohol or removal of H and O in the ratio 2:1 from a compound/molecule/alcohol 1
(do not credit "from a substance")
(do not credit "removal of water molecules" unless qualified from a compound/molecule etc.)

M2: Catalyst = concentrated H_2SO_4 or concentrated/oily/syrupy phosphoric acid or aluminium oxide/ pumice/porous pot 1

M3: $CH_3CH_2OH \longrightarrow H_2C{=}CH_2 + H_2O$ 1
(credit use of C_2H_5OH)
(penalise use of C_2H_6O here unless already penalised in part(a). Possible credit as repeat error)
(credit C_2H_4 and $CH_2{=}CH_2$ for ethene, but penalise CH_2CH_2, $CH_2.CH_2$, $CH_2{:}CH_2$)
(ignore H_2SO_4 if it appears on both sides of equation)

(c) M1: large(r) to small(er) molecules/hydrocarbons/compounds or high(er) Mr alkanes to low(er) Mr alkanes (+ alkenes) (+ H_2) 1

M2: breakage/homolysis/splitting of C-C/carbon chain/carbon skeleton 1
(do not credit breaking C-H bonds alone, but ignore if accompanied by C-C)

M3: reactive intermediate is (free/alkyl) radical or radical mechanism 1
(do not credit "free radical substitution" and penalise M3 as a contradiction if mentioned with free radical intermediates)

M4: any T (or range) in the range 400 to 900^{o}C or high temperature 1
(*ignore "pressure")*

M5: $CH_3CH_2CH_2CH_3$ (*OR* C_4H_{10}) $\longrightarrow$ $H_2C{=}CH_2$ + CH_3CH_3 (*OR* C_2H_6) 1
or $CH_3CH_2CH_2CH_3$ (*OR* C_4H_{10}) $\longrightarrow$ $2H_2C{=}CH_2$ + H_2
(credit C_2H_4 and $CH_2{=}CH_2$ for ethene, but penalise CH_2CH_2, $CH_2.CH_2$, $CH_2{:}CH_2$ and note possible RE from part(b))

Total 15

General principles applied to marking CHM3/W papers (updated January 2006)

It is important to note that the guidance given here is generic and specific variations may be

made at individual standardising meetings in the context of particular questions and papers.

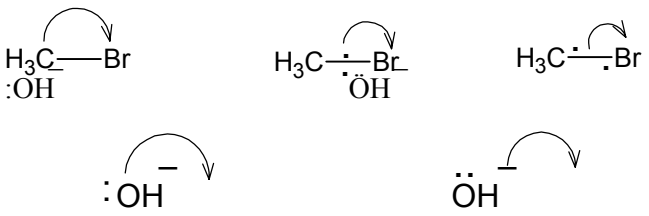
Errors which should be penalised

Each of the following illustrates an error which should be penalised once only **per script.**

On the second occasion that the **same error** is repeated for the same bond or species, the mark should be awarded and the tick annotated **RE** (repeat error).

A. Mechanisms

1. Curly arrows should originate either from a lone pair of electrons or from a bond. Each of the following representations should be **penalised once** per script.



2. The absence of a radical dot in a free radical substitution should be **penalised once** per script.

3. The use of double-headed arrows or the incorrect use of half-headed arrows in a free-radical mechanisms will be **penalised once** only per script. In general, there is no expectation for candidates to use half –headed arrows.

B. Structures

1. Bonds should be drawn clearly between the relevant atoms. By way of illustration, each of the following representations should be **penalised once** per script.

(accept up to the mid-point)

If candidates show the alcohol functional group as C-H-O, they may be penalised on every occasion.

Some latitude may be given to the representation of C-C bonds in structures, given that CH_3─ is considered to be interchangeable with H_3C─ , even though the latter would be preferred.
Poor presentation of vertical C-C bonds may be penalised.

2. Formulae for specific compounds which should be **penalised**.

CH_3COH	for	ethanal
CH_2OCH_2 or CH_2CH_2O	for	epoxyethane
CH_3CH_2HO $OHCH_2CH_3$ C_2H_6O	for	ethanol
CH_2CH_2 $CH_2.CH_2$ $CH_2:CH_2$	for	ethene

(N.B. Exceptions may be made in the context of balancing equations)

3. The use of 'sticks' in structures should be **penalised once** per script. This will also apply to structures in mechanisms.

C. Names

As a general principle, non-IUPAC names or incorrect spelling or incomplete names should be **penalised once** per script. Some illustrations are given here. *(N.B. specific exceptions may be made at individual standardising meetings)*

but-2-ol 2-hydroxybutane butane-2-ol 2-butanol	all should be **butan-2-ol**
2-methpropan-2-ol	should be **2-methylpropan-2-ol**
2-methylbutan-3-ol	should be **3-methylbutan-2-ol**
3-methylpentan 3-mythylpentane	both should be **3-methylpentane**
propanitrile	should be **propanenitrile**

aminethane should be **ethylamine** (although aminoethane may gain credit)

D. Reagents

The guiding principle is that a reagent is a chemical which can be taken out of a bottle or container. Failure to identify whole reagents will be penalised.

cyanide (ion) **should be e.g. potassium cyanide**

hydroxide (ion) **should be e.g. sodium hydroxide**

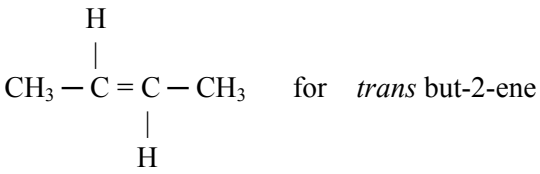
Some general guidance on organic structures

Each of the following **should be given credit** as alternatives to correct representations of the structures.

$CH_2 = CH_2$ for ethene, $H_2C=CH_2$

$CH_3CHOHCH_3$ for propan-2-ol, $CH_3CH(OH)CH_3$

CH_2OHCH_2OH for ethane-1,2-diol



for *trans* but-2-ene