M11/4/CHEMI/HP3/ENG/TZ2/XX/M



International Baccalaureate® Baccalauréat International Bachillerato Internacional

# MARKSCHEME

## May 2011

# CHEMISTRY

**Higher Level** 

Paper 3

18 pages

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### **General Marking Instructions**

### Subject Details: Chemistry HL Paper 3 Markscheme

### **Mark Allocation**

Candidates are required to answer questions from TWO of the options [2 x 25 marks]. Maximum total = [50 marks].

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- 1. A markscheme often has more marking points than the total allows. This is intentional. Do not award more than the maximum marks allowed for part of a question.
- 2. Each marking point has a separate line and the end is signified by means of a semicolon (;).
- 3. An alternative answer or wording is indicated in the markscheme by a slash (/) either wording can be accepted.
- 4. Words in brackets ( ) in the markscheme are not necessary to gain the mark.
- 5. Words that are <u>underlined</u> are essential for the mark.
- 6. The order of marking points does not have to be as in the markscheme, unless stated otherwise.
- 7. If the candidate's answer has the same "meaning" or can be clearly interpreted as being of equivalent significance, detail and validity as that in the markscheme then award the mark. Where this point is considered to be particularly relevant in a question it is emphasized by writing *OWTTE* (or words to that effect).
- 8. Occasionally, a part of a question may require an answer that is required for subsequent marking points. If an error is made in the first marking point then it should be penalized.
- 9. Only consider units at the end of a calculation.
- 10. Significant digits should only be considered in the final answer. Deduct 1 mark in the paper for an error of 2 or more digits unless directed otherwise in the markscheme.

*e.g.* if the answer is 1.63: 2 *reject* 1.6 accept 1.63 accept 1.631 accept 1.6314 *reject* 

- **11.** If a question specifically asks for the name of a substance, do not award a mark for a correct formula, similarly, if the formula is specifically asked for, do not award a mark for a correct name.
- **12.** If a question asks for an equation for a reaction, a balanced symbol equation is usually expected, do not award a mark for a word equation or an unbalanced equation unless directed otherwise in the markscheme.
- 13. Ignore missing or incorrect state symbols in an equation unless directed otherwise in the markscheme.

**Option A** — Modern analytical chemistry

A1.	(a)	radio	(wave);	[1]
	(b)	(mol	owave: ecular) rotation; ot allow mark if incorrect rotations (i.e. not molecular) are stated.	
			<i>aviolet:</i> ronic transition;	[2]
	(c)	IR ir <sup>1</sup> H N	volves vibrations of bonds / IR involves shorter wavelength/more energy than MR;	
			eas <sup>1</sup> H NMR involves transitions between different energy states in the nucleus h are lower in energy / <sup>1</sup> H NMR occurs in the radio region therefore energy is r;	[2]
A2.	(a)	(stret	cches/vibrations in) HBr involve change in bond dipole / (stretches/vibrations in)	
		Br <sub>2</sub>	do not involve change in bond dipole;	[1]
	(b)	(i)	C=O / carbonyl;	[1]
		(ii)	m/z = 102: molecular parent ion / (CH <sub>3</sub> ) <sub>3</sub> CCOOH <sup>+</sup> / C <sub>5</sub> H <sub>10</sub> O <sub>2</sub> <sup>+</sup> / M <sup>+</sup> ;	
			$m/z = 57$ : $(CH_3)_3 C^+ / (M - COOH)^+ / C_4 H_9^+$ ; Penalize missing + once only.	[2]
		(iii)	(H of) COOH group;	[1]
		(iv)	nine hydrogens in the same environment / $(CH_3)_3C$ – (group);	[1]
		(v)	$(CH_3)_3CCOOH/(CH_3)_3CCO_2H/H_3C - C - OH;$	
			CH <sub>3</sub>	[1]
		(vi)	Number of peaks: 2; Ratio of peak areas: 1:9 / 9:1; Splitting patterns: two singlets / no splitting;	[3]
		(vii)	Number of peaks: 4; Ratio of peak areas: 3:2:2:3;	[*]
			Accept in any order. Splitting patterns: two triplets <b>and</b> two quartets;	[3]

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A3. human body consists of 70 %/mostly/a lot of water; protons in water molecules/in carbohydrates, proteins and fats can be detected by MRI; water in different environments; organs have different water to lipid ratios; so that protons have different environments so produce different effects; [2 max]
A4. sample vaporized/heated; assumes sample does not decompose at high temperature; different components carried through apparatus in stream of carrier gas; mobile phase inert gas/nitrogen/helium/argon;

stationary phase liquid/long chain alkane/hydrocarbon/grease adsorbed on solid support; each component has a different attraction for the hydrocarbons / attraction of components depends on molecular mass and polarity;

less volatile components have longer retention time / components pass through at different rates / *OWTTE*;

components detected by flame ionizer;

converted to electrical current / connected to chart recorder / connected to mass spectrophotometer/spectrometer; [5 max]

### **Option B** — Human biochemistry

<b>B1.</b>	(a)	<b>X</b> is glycerol/propane-1,2,3-triol/ $CH_2(OH)CH(OH)CH_2(OH)$ ;	
		$Y$ is water/ $H_2O$ ;	[2]
	(b)	$CH_2OOC(CH_2)_6CH_3$	
		$CHOOC(CH_2)_{10}CH_3$	
		$CH_2OOC(CH_2)_{16}CH_3;$	[1]
		Accept the fatty acids in any order.	
	(c)	colid as contains (three) saturated/straight fatty acid chains; can pack closer together;	
		nave stronger London/dispersion/van der Waals' forces between chains;	[3]
	(d)	esterification / condensation;	[1]
B2.	(a)	i) organic dye / ninhydrin;	[1]
		ii) glutamic acid/Glu;	
		isoelectric point is below pH of buffer / acts as an acid / loses H <sup>+</sup> ; becomes negatively charged;	[3]
		<li>balanced (positive and negative) charges / no overall charge / zwitterion; amphoteric / buffer solution;</li>	[1 max]
	(b)	$H_2NCH_2COOH + H^+ \rightleftharpoons H_3N^+CH_2COOH / H_3N^+CH_2COO^- + H^+ \rightleftharpoons H_3N^+CH_2COO^-$	CH <sub>2</sub> COOH;
		$H_2NCH_2COOH + OH^- \rightleftharpoons H_2NCH_2COO^- + H_2O /$	
		$H_3N^+CH_2COO^- + OH^- \rightleftharpoons H_2NCH_2COO^- + H_2O;$	[2]
		$Accept \rightarrow instead \ of \rightleftharpoons$	

<b>B3</b> .	$C_6H_{12}O_6 + 6H_2O \rightarrow 6CO_2 + 24H^+ + 24e^-;$	
	$Cu^{2+} + e^- \rightarrow Cu^+;$	[2]
	Accept e instead of $e^-$ .	

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B4.	(a)	(i)	ribose (in RNA) <b>and</b> deoxyribose (in DNA); deoxyribose lacks an oxygen atom (on C2) / ribose has an OH group on second carbon in ring while deoxyribose has only H;	[2]
		(ii)	DNA contains thymine and RNA contains uracil / DNA is a double-strand nucleic acid and RNA is a single-strand nucleic acid / <i>OWTTE</i> ;	
	(b)	(i)	restriction enzymes used to break DNA into small fragments; fragments are subjected to electrophoresis; portions of DNA placed on gel; electric field/voltage applied; negatively charged portions of DNA migrate to positive electrode; DNA portions separated by size / small portions of DNA travel further through the gel; DNA sequences stained; observed under UV light;	[5 max]
		(ii)	paternity cases / forensic cases;	[1]

### **Option C** — Chemistry in industry and technology

C1.	(a)	(i)	melting point of the cryolite solution is much lower than the melting point of alumina/Al <sub>2</sub> O <sub>3</sub> / it lowers the melting point of the mixture / cell operates at lower temperature; Allow lowers melting point or lowers melting point of aluminium oxide. Do not allow lowers melting point of aluminium.	[1]
		(ii)	$2O^{2-} \rightarrow O_2 + 4e^- / O^{2-} \rightarrow \frac{1}{2}O_2 + 2e^-;$	[1]
			Allow $e$ instead of $e^-$ .	
	(b)		of fossil fuels (to provide energy); ation of the (graphite) positive electrode/anode;	[2]
C2.	(a)	(i)	reactants are adsorbed onto the surface of the catalyst; bonds are weakened so molecules are more likely to react / collisions with correct orientation occur more frequently;	[2]
		(ii)	only effective on the surface / get poisoned / forms clumps / efficiency/surface area decreases over time;	[1]
	(b)	effic shou work shou cost	ld produce only the desired product / selectivity; iency; ld be able to work under both mild and severe conditions / should be able to c at high temperatures; ld not produce an (unwanted) environmental impact; / economic viability / <i>OWTTE</i> ; of poisoning/contamination;	[2 max]
	(c)	(i)	production of high density polyethene / production of polymers of 1-alkenes / polymerization;	[1]
		(ii)	a transition metal / Ti / Ti(IV) chloride / V; and a main group metal alkyl compound / aluminium alkyl / $(C_2H_5)_3Al$ ;	[2]

C3.	(a)	incre beco	shaped) molecules aligned in the same direction; easing temperature causes arrangement to lose its directional order/molecules to me more randomly arranged; normal liquid state occurs;	) [3]
	(b)	liqui mole	tance should be chemically stable; d-crystal phase should be stable over a suitable range of temperatures; ecules should be polar; e should be a rapid change in direction/fast switching speed;	[3 max]
	(c)	(i)	lyotropic liquid crystal; rigid rod-shaped molecules; alignment of molecules depends on concentration of solution;	[3]
		(ii)	(Kevlar has) strong hydrogen bonds between chains; creating a very ordered/strong structure;	[2]
		(iii)	acid donates a proton to the O and N atoms; breaking the hydrogen bonds;	[2]

**Option D** — Medicines and drugs

D1.	(a)	fast delivery / OWTTE;	[1]
	(b)	diamorphine has (2) ester/acetyl/COOCH <sub>3</sub> groups instead of hydroxyl/OH groups; diamorphine is less polar/non-polar;	[2]
D2.	(a)	anxiety; irritability/restlessness; sleeplessness; increased urine output/diuretic; trembling/shaking; increased heart rate/tachycardia;	[2 max]
	(b)	(i) amide;	[1]
		(ii) (tertiary) amine;	[1]
D3.	(a)	if concentration is too high it will have harmful side effects / determination of the lethal dose (to 50 % of the population) / <i>OWTTE</i> ; if concentration is too low it has little or no beneficial effect / determination of the	

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if concentration is too low it has little or no beneficial effect / determination of the effective dose / dose which has a noticeable effect (on 50 % of the population) / *OWTTE*;

the rapeutic window is the range between these doses / range over which a drug can be safely administered / ratio of  $LD_{50}$ ;  $ED_{50}$ ;

for minor ailments a larger window is desirable, for serious conditions a smaller window may be acceptable / *OWTTE*;

(therapeutic window) depends on the drug/age/sex/weight; a small therapeutic window means that an overdose is a high risk / *OWTTE*; [4 max]

- (b) placebo contains none of the compound being tested as a drug; placebo can "fool" the body into healing itself / OWTTE; placebo is used as a control to measure the effectiveness of a drug / OWTTE; half/some of trial group given placebo and half/some given drug; patients and administrators should not know who gets a placebo and who gets a drug / double blind trial; [3 max]
- (c) LD<sub>50</sub> / ED<sub>50</sub>;
   risk:benefit ratio;
   side-effects;
   tolerance;
- (d) chirality / optical isomerism / two different enantiomers;
   each enantiomer must be tested for side effects / modern drugs may have only one
   enantiomeric form / OWTTE;

[1 max]

(e)	(i) (ii)	reagents; (to produce) a large number of products; mix-and-split technique; small amounts of compounds are attached to resin/beads; library of many different but related compounds; compounds are tested for biological activity/effectiveness as possible drugs; parallel synthesis can produce smaller, more focused libraries;	[3 max]
(a)	both both	are amines; contain an indole ring;	
	psilo psilo	bcybin has ionic ends / is a zwitterion; bcybin contains P/phosphate group;	[2 max]
(b)	enha loss conf	anced auditory and visual perception / hallucinations; of sense of time;	[2 max]
	(a)	<ul> <li>(ii)</li> <li>(ii)</li> <li>(a) Simulation</li> <li>both</li> <li>both<td><ul> <li>automated process reacts a small number of compounds with a variety of reagents;</li> <li>(to produce) a large number of products;</li> <li>mix-and-split technique;</li> <li>small amounts of compounds are attached to resin/beads;</li> <li>library of many different but related compounds;</li> <li>compounds are tested for biological activity/effectiveness as possible drugs;</li> <li>parallel synthesis can produce smaller, more focused libraries;</li> <li>(ii) purification of the product is relatively easy / product can be isolated by washing and filtration;</li> <li>(a) <i>Similarities: [1 max]</i></li> <li>both are amines;</li> <li>both contain a indole ring;</li> <li>both contain a benzene ring;</li> <li><i>Differences: [1 max]</i></li> <li>psilocybin has ionic ends / is a zwitterion;</li> <li>psilocybin contains P/phosphate group;</li> <li>LSD contains an amide group;</li> <li>(b) feelings of relaxation/euphoria;</li> <li>enhanced auditory and visual perception / hallucinations;</li> <li>loss of sense of time;</li> <li>confusion / emotional distress;</li> </ul></td></li></ul>	<ul> <li>automated process reacts a small number of compounds with a variety of reagents;</li> <li>(to produce) a large number of products;</li> <li>mix-and-split technique;</li> <li>small amounts of compounds are attached to resin/beads;</li> <li>library of many different but related compounds;</li> <li>compounds are tested for biological activity/effectiveness as possible drugs;</li> <li>parallel synthesis can produce smaller, more focused libraries;</li> <li>(ii) purification of the product is relatively easy / product can be isolated by washing and filtration;</li> <li>(a) <i>Similarities: [1 max]</i></li> <li>both are amines;</li> <li>both contain a indole ring;</li> <li>both contain a benzene ring;</li> <li><i>Differences: [1 max]</i></li> <li>psilocybin has ionic ends / is a zwitterion;</li> <li>psilocybin contains P/phosphate group;</li> <li>LSD contains an amide group;</li> <li>(b) feelings of relaxation/euphoria;</li> <li>enhanced auditory and visual perception / hallucinations;</li> <li>loss of sense of time;</li> <li>confusion / emotional distress;</li> </ul>

Opt	<b>Option E</b> — Environmental chemistry					
E1.	(a)	N <sub>2</sub> O; artificial fertilizers / combustion/decomposition of biomass;				
	Award [2 max] for one of the following pairs. $H_2O$ ; evaporation of oceans/lakes;					
		OR				
		SF <sub>6</sub> ; insulator in electrical industry;				
		OR				
		O <sub>3</sub> ; photochemical smog / electrical generators; [4 max]				
		Allow correct names (e.g. ozone) instead of formulas. Sources must match gases for [1].				
	(b)	breakdown of grass in animals stomachs / microbes in animals stomachs / by-product of fermentative digestion in rumen (and hind gut); [1]				
	(c) seasonal since plants grow in spring and decay in autumn/fall / amount of CO <sub>2</sub> in the atmosphere depends on (natural processes such as) photosynthesis, which happens (more) in spring and summer than in autumn/fall and winter;					
	(d)	rise in sea levels / thermal expansions of the oceans; melting polar ice-caps/glaciers; changes in climatic patterns / <i>OWTTE</i> ; changes in agriculture and bio-distribution / <i>OWTTE</i> ; [1 max] <i>Allow specific changes.</i>				
E2.	<ul> <li>(a) Mercury: batteries / fungicides/seed dressings / electrolysis of brine/manufacture of chlorine/sodium hydroxide / dental amalgams / paints; Allow pesticides.</li> <li>PCBs: capacitors / transformers / other electrical equipment / plasticizers / adhesive</li> </ul>					
		industries; [2]				

(b) Multi-Stage Distillation: sea water is heated to its boiling point / water vaporizes; condensation of pure water / water free of impurities; heat given off by condensing water saves energy; Reverse Osmosis: high pressure / greater than osmotic pressure / 70 atm; uses partially/semi-permeable membrane; water passes through leaving salts behind; high energy cost to achieve pressure needed / OWTTE; [5 max]  $K_{\rm sp} = [{\rm Ag}^+][{\rm Cl}^-]/1.8 \times 10^{-10} = 8.0 \times 10^{-3} \times [{\rm Cl}^-];$ **E3.** (a)  $[Cl^{-}] = 2.3 \times 10^{-8} \text{ mol dm}^{-3};$  $K_{\rm sp} = [{\rm Pb}^{2+}] [{\rm Cl}^{-}]^2 / 1.7 \times 10^{-5} = 1.9 \times 10^{-2} \times [{\rm Cl}^{-}]^2;$  $[Cl^{-}] = 3.0 \times 10^{-2} \text{ mol dm}^{-3};$ AgCl will precipitate first (because it is less soluble); [5] (b) (i) amount/number of exchangeable cations in clay / OWTTE; [1] (ii) enhances ability of soil to buffer changes (in pH) / OWTTE;

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- binds to organic and inorganic compounds in soil / nutrients not washed away easily / *OWTTE*; forms stable complexes with cations / can absorb heavy metal cations and prevent them from being absorbed by plants; reduces negative environmental effects of pesticides, heavy metals and other pollutants by binding contaminants; increases CEC of soil; [2 max]
- (iii) Nitrogen: most available when pH nearly neutral; in highly acidic or alkaline soils, little breakdown of nitrogen; plants become starved for nitrogen under these conditions (even with lots of fertilizer);

*Phosphorus:* most available at low pH; phosphates insoluble at high pH;

[3 max]

Award [1] for nitrogen and [1] for phosphorus and [1] for any other marking point.

[2 max]

### **Option F** — Food chemistry

F1.	(a)	(i)	(component) fatty acids;	
			glycerol/propane-1,2,3-triol/CH <sub>2</sub> (OH)CH(OH)CH <sub>2</sub> (OH);	[2]

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- (ii) (presence of) enzymes/lipase; heat; moisture;
- (iii) nitrogen excludes oxygen; foil pack excludes light; oxygen/light increases the rate of oxidation; fatty acid chains are oxidized / oxygen adds across C=C double bond of unsaturated fatty acid / produces aldehydes and ketones; [3 max]
- *Initiation*:  $RH \rightarrow R \cdot + H \cdot$ ; (b)

*Propagation*:  $R \bullet + O_2 \rightarrow ROO \bullet / ROO \bullet + RH \rightarrow R \bullet + ROOH$ ;

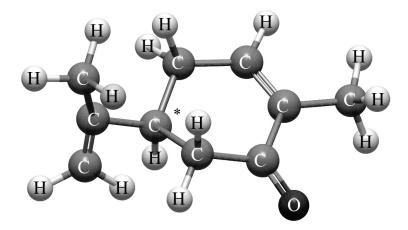
*Termination*:  $\mathbb{R} \cdot + \mathbb{R} \cdot \rightarrow \mathbb{R}\mathbb{R} / \mathbb{R} \cdot + \mathbb{ROO} \cdot \rightarrow \mathbb{ROOR} / \mathbb{ROO} \cdot + \mathbb{ROO} \cdot \rightarrow \mathbb{ROOR} + \mathbb{O}_2$ ; [3] Allow R instead of R• etc.

F2.	(a)	(i)	OH is readily oxidized (in preference to the food); OH/phenol are free radical scavengers; conjugate base formed is stabilized by resonance; large (conjugated) Pi system; <i>Allow reducing agents</i> .	[1 max]
		(ii)	lower levels of LDL cholesterol; lower blood sugar levels; reduce high blood pressure; prevent development of cancer;	[2 max]
	(b)	(i)	quinoidal base + H <sup>+</sup> $\rightleftharpoons$ flavylium cation / QB + H <sup>+</sup> $\rightleftharpoons$ FC <sup>+</sup> ; Accept $\rightarrow$ instead of $\rightleftharpoons$	[1]
		(ii)	blueberries are acidic <b>and</b> H <sup>+</sup> ions react with aluminium to form Al <sup>3+</sup> ; Al <sup>3+</sup> ions form (deeply) coloured (coordination) complexes with anthocyanins; fruit discoloured; Al <sup>3+</sup> cause health problems / Al <sup>3+</sup> deposited in bones instead of Ca <sup>2+</sup> ;	[2 max]
	(c)		contain planar heterocyclic unit/porphyrin; ugated double bonds (in cyclic system) / alkene (groups);	
			<i>brophyll:</i> chlorophyll has magnesium/ester (groups)/R-group on C3/long hydrocarbor n;	1

*Heme:* only heme has carboxylic acid (groups)/iron; identification of chiral centre \*;

F3.

(a)



- [1]
- (b) *R*, *S* notation represents absolute configuration (around chiral centre/stereocentre);
   *d*, *l* notation represents direction of plane of polarized light; [2]

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(c) priority given to each atom (group) around chiral centre with hydrogen having lowest priority (pointing away); other groups from highest to lowest atomic number arranged in counterclockwise direction; [2]
 Marks may also be scored from numbered groups on diagram around chiral centre.

# Option G — Further organic chemistry G1. (a) 1,3-cyclohexadiene; [1] (b) addition reactions not favoured energetically since this would involve disruption of cloud of delocalized electrons / stabilization energy would need to be supplied and product would lack delocalized ring of electrons making it less stable / OWTTE; [1] (c) For chloromethylbenzene: electron deficient carbon on -CH<sub>2</sub>Cl group making it susceptible to nucleophilic attack; For chlorobenzene: steric hinderance / repulsion by electron cloud in benzene ring/C–Cl less polar;

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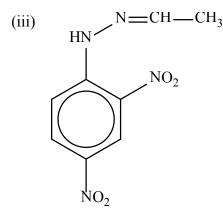
 C-Cl bond stronger;
 [2 max]

 Award [1] mark for either of the above.

### **G2.** (a) (i) $H_3CCHClCH_2I$ ;

(ii)  $H_3CC(OH)(CN)H$ ; [1]

;



[1]

[1]

[1]

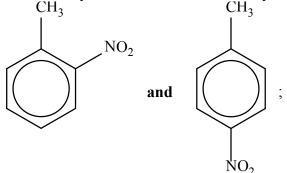
- (iv)  $(CH_3)_2 CHOH$ ; [1]
- (b)  $CH_3CHICH_2CI;$

(c)	Reaction	Туре
	(a) (i)	electrophilic addition;
	(a) (ii)	nucleophilic addition;
	(a) (iii)	addition-elimination;
	(a) (iv)	Grignard;

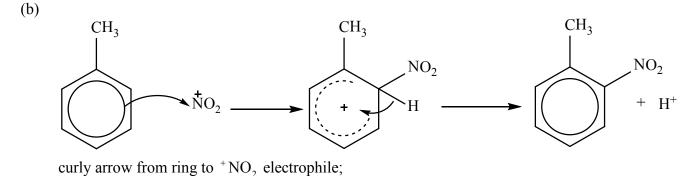
[4]

**G3.** (a) (i) CH<sub>3</sub>CONHCH<sub>2</sub>CH<sub>3</sub> and HCl; Allow corresponding names also.

(ii) 2-nitromethylbenzene and 4-nitromethylbenzene /



Allow use of ortho and para notation.



curly arrow from ring to  $NO_2$  electrophile; drawing of intermediate structure with + on ring; curly arrow from C–H to +; *Allow corresponding mechanism for formation of para isomer. Allow corresponding mechanism involving Kekulé notation.* 

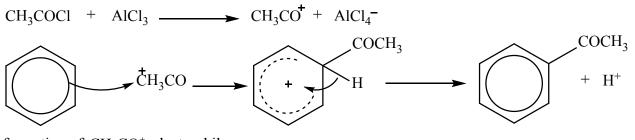


[4]

[1]

[1]

### **G4**.



formation of  $CH_3CO^+$  electrophile; curly arrow from ring to  $CH_3CO^+$  electrophile; curly arrow from CH to + in ring; formation of  $C_6H_5COCH_3$  and  $H^+$ ; *Allow corresponding mechanism involving Kekulé notation*. **G5.** *Step 1:* 

H<sub>3</sub>PO<sub>4</sub>/phosphoric acid / H<sub>2</sub>SO<sub>4</sub>/sulfuric acid;

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*Product from step 1:* CH<sub>3</sub>CH<sub>2</sub>CH=CH<sub>2</sub>/but-1-ene;

Step 2: Br<sub>2</sub> /bromine;

[3]