Give the marks for the points in the marking scheme; an answer in other words that says the same is right.

1 Reading a rate law: two bromides

a. ANSWER A · 8

Tests: deciding SN1 or SN2 from the rate law, not from a label; Unit 3's initial rates and first-order half-life.

i. P: doubling [P] (run 1 → 2) doubles the rate, and doubling [OH^-] (1 → 3) doubles it too: first order in each, **rate = k[P][OH^-]**, second order overall. Q: doubling [Q] (4 → 5) doubles the rate, doubling [OH^-] (4 → 6) leaves it unchanged: first order in Q, zero order in OH^-, **rate = k[Q]**.

ii. OH^- takes part in P's slow step: a one-step backside attack, **SN2**, which needs an open carbon: P is **1-bromobutane** (primary). OH^- is not in Q's slow step: the bromide ionizes on its own and OH^- joins the carbocation afterwards, **SN1**, which needs a stable carbocation: Q is **2-bromo-2-methylpropane** (tertiary).

iii. k = rate/[Q] = $2.0 \times 10^{-5}/0.010$ = **2.0×10^{-3} s^{-1}**. $t_{1/2}$ = 0.693/k = 347 s; 75% reacted is two half-lives, **693 s (about 11.6 min)**. In run 6 **the same, 693 s**: the rate doesn't depend on [OH^-], and a first-order half-life doesn't depend on $[Q]_0$ either. The tempting answer, "faster with twice the hydroxide", is what P would do, not Q.

iv. P: **4 times** (2 × 2). Q: **2 times** (only the doubled bromide counts).

(The rates are made up, of a size that suits the two mechanisms.)

MARKING SCHEME

- ✓ P first order in P and in OH^-: rate = k[P][OH^-].
- ✓ Q first order in Q, zero order in OH^-: rate = k[Q].
- ✓ P is SN2 (OH^- in the one slow step), so P is the primary 1-bromobutane.
- ✓ Q is SN1 (ionization alone is slow, needs a stable carbocation), so Q is the tertiary 2-bromo-2-methylpropane.
- ✓ k = 2.0×10^{-3} s^{-1}.
- ✓ 75% takes two half-lives, 693 s.
- ✓ Run 6 also 693 s, because the rate is independent of [OH^-].
- ✓ P's rate × 4, Q's × 2.

b. ANSWER HA · 3

Tests: what "not in the rate law" means for SN1 (the nucleophile reacts, but after the slow step), and E1 sharing SN1's first step.

The slow step, Q → $(CH_3)_3C^+ + Br^-$, needs no OH^-, so Q ionizes **at the same rate** as in run 4 (rate = k[Q]). The carbocation is then caught by whatever has a lone pair: **water**, giving $(CH_3)_3C–OH$, 2-methylpropan-2-ol, and **ethanol**, giving the ether $(CH_3)_3C–O–CH_2CH_3$; or a solvent molecule takes a β-hydrogen (E1), giving **2-methylpropene**. HBr forms instead of NaBr, so the solution turns **acidic**. Sandesh's mistake: a rate law tells you what takes part in the slow step, not what takes part in the reaction.

MARKING SCHEME

- ✓ Same rate as run 4: the slow ionization doesn't involve OH^-.
- ✓ The carbocation is caught by water (2-methylpropan-2-ol) or ethanol (the ether), or loses H^+ to give 2-methylpropene (E1).
- ✓ HBr forms, so the solution becomes acidic.

2 What the polarimeter shows

ANSWER

Tests: inversion and racemization as measured evidence; a polarimeter reading turned into a composition; the slight excess of the inverted product in SN1.

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i. Run 1 gives only the mirror-image arrangement (+13.5°, the full value): **complete inversion**, the mark of **SN2** (a strong nucleophile at a high concentration, in a solvent that is mostly acetone, and a secondary carbon open enough to reach). Run 2 gives a nearly inactive product: **mostly racemization**, through a flat carbocation, **SN1** (water and ethanol steady the ions, and Ag^+ pulls the bromide off; no strong nucleophile is there). HA · 5

ii. A racemic mixture rotates 0°, so only the excess of one form rotates: 1.6/13.5 = 0.119, an excess of 11.9% of the + form (the inverted one). So (100 + 11.9)/2 = **55.9% inverted (+)** and **44.1% the same arrangement as A (−)**. Not 50 : 50 because the bromide ion, just after it leaves, still shields the face it left from, so water reaches the carbocation a little more often from the other side: the excess is the **inverted** form, never the retained one.

iii. **No.** A and butan-2-ol are different compounds, and the sign of rotation of one says nothing about the arrangement of the other. The evidence for inversion is the comparison with butan-2-ol's own two forms: +13.5° is the form with the opposite arrangement to A. (The rotations are made up for the problem.)

MARKING SCHEME

- ✓ Run 1: complete inversion, SN2.
- ✓ Run 2: mostly racemization through a flat carbocation, SN1.
- ✓ 55.9% inverted, 44.1% retained (excess 11.9%).
- ✓ The leaving bromide shields its own face, so the inverted form is in excess.
- ✓ The signs of two different compounds can't be compared; only the alcohol's own forms show inversion.

3 The four bromides C_4H_9Br

a. **ANSWER** A · 5

Tests: putting the unit's tests together: SN1 speed with $AgNO_3$ (3° > 2° > 1°), chirality, the kinds of β-hydrogen in an elimination (Saytzeff), the iodoform test.

- The silver nitrate test sorts them by carbocation stability: Z is **tertiary**, X **secondary**, W and Y **primary**. The only tertiary one is **Z = 2-bromo-2-methylpropane**, $(CH_3)_3CBr$; the only secondary one is **X = 2-bromobutane**, $CH_3CH_2CHBrCH_3$ (and it has the chiral carbon, as its activity says).
- Z can lose an H only from a CH_3, giving **2-methylpropene**, $(CH_3)_2C{=}CH_2$. The primary bromide that gives the same alkene has the same branched chain: **Y = 1-bromo-2-methylpropane**, $(CH_3)_2CHCH_2Br$ (its only β carbon is C-2). So **W = 1-bromobutane**, which gives only **but-1-ene**.
- X has β-hydrogens on C-1 and C-3: **but-2-ene** (major, the more substituted, Saytzeff) and but-1-ene.

MARKING SCHEME

- ✓ Z is 2-bromo-2-methylpropane (tertiary, fastest with $AgNO_3$).
- ✓ X is 2-bromobutane (secondary, chiral).
- ✓ Y is 1-bromo-2-methylpropane (gives the same alkene as Z, 2-methylpropene).
- ✓ W is 1-bromobutane, giving but-1-ene.
- ✓ X gives but-2-ene as the major alkene (Saytzeff), with some but-1-ene.

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b. ANSWER HA · 3

Tests: judging which evidence is needed; the iodoform test needs $CH_3CH(OH)–$, which a tertiary alcohol doesn't have.

i. **The optical activity and the iodoform result.** The silver nitrate test alone fixes Z (the only tertiary bromide) and X (the only secondary one); of the two primary ones, the alkene finding picks Y as the one giving Z's alkene, leaving W. X's optical activity and the iodoform test only confirm it: 2-bromobutane has the chiral carbon, and butan-2-ol the $CH_3CH(OH)–$ group.

ii. **No.** Z's alcohol is 2-methylpropan-2-ol, $(CH_3)_3C–OH$. The test needs $CH_3CO–$ or a $CH_3CH(OH)–$ that iodine can oxidize to $CH_3CO–$; the carbinol carbon of a tertiary alcohol has **no hydrogen** to lose, so it can't become a C=O, and no iodoform forms.

MARKING SCHEME

- ✓ Optical activity and iodoform: silver nitrate fixes Z and X, and the alkenes tell Y from W.
- ✓ No: 2-methylpropan-2-ol has no H on the carbon carrying OH.
- ✓ So it can't be oxidized to $CH_3CO–$, and gives no iodoform.

4 One alkene, not two

a. ANSWER A · 3

Tests: Saytzeff's rule used to choose a starting material; elimination against substitution.

1-Bromobutane. Its α carbon (C-1) has only one β carbon, C-2, so it can give only **but-1-ene**. 2-Bromobutane has β-hydrogens on C-1 and C-3 and gives mainly **but-2-ene** (about 80%, the more substituted alkene), the wrong product, with only about 20% but-1-ene to separate. What she gives up: a primary bromide eliminates less readily than a secondary one, and some of it is substituted instead (giving butan-1-ol or an ether with the ethanol), so the **yield is lower, but the alkene is pure**.

MARKING SCHEME

- ✓ 1-Bromobutane: one kind of β-hydrogen, so only but-1-ene.
- ✓ 2-Bromobutane gives mainly but-2-ene (Saytzeff).
- ✓ The cost: a primary bromide eliminates less easily, so a lower yield (some substitution).

b. ANSWER HA · 3

Tests: substitution against elimination for a tertiary halide; choosing the Grignard route to a tertiary alcohol.

He will get mostly **2-methylpropene**: alcoholic KOH is a strong base, and a tertiary halide, crowded at its α carbon, readily loses HBr (E2), so elimination wins. Better ways: boil the bromide with **aqueous** KOH or simply with water, where it reacts by SN1 and water catches the carbocation (some alkene still forms by E1, from the same carbocation); or, cleanest, build the alcohol so there is nothing to eliminate: **propanone + methylmagnesium bromide** (made from bromomethane and magnesium in dry ether), then water: a ketone and a Grignard reagent give a tertiary alcohol, $(CH_3)_2C(OH)CH_3$, with no haloalkane at a tertiary carbon to eliminate.

MARKING SCHEME

- ✓ Mostly 2-methylpropene.
- ✓ A strong base with a crowded tertiary halide favors elimination over substitution.
- ✓ A better way: aqueous KOH or water (SN1, some alkene still), or propanone + CH_3MgBr in dry ether, then water.

5 Building a longer chain

a. ANSWER

Tests: counting carbons: which reaction adds how many (CN^- +1, Grignard with HCHO +1, Grignard with R′CHO joins two pieces, NH_3 none).

i. Two carbons to three: add one as cyanide, then hydrolyze it.

$$CH_3CH_2Br \xrightarrow{KCN(alc)} CH_3CH_2CN \xrightarrow[\Delta]{H_2O/H^+} CH_3CH_2COOH$$

ii. Four carbons with N at the end. The tempting routes fall short: NH_3 on bromoethane gives ethanamine (2 C), and KCN then $LiAlH_4$ gives propan-1-amine (3 C). So first add one carbon by Grignard and methanal, keeping an OH to turn into a halide, then add the fourth as cyanide and reduce it:

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$$CH_3CH_2Br \xrightarrow[\text{dry ether}]{Mg} CH_3CH_2MgBr \xrightarrow[2.\ H_2O]{1.\ HCHO} CH_3CH_2CH_2OH \xrightarrow[\Delta]{PBr_3} CH_3CH_2CH_2Br$$ A · 6

$$CH_3CH_2CH_2Br \xrightarrow{KCN(alc)} CH_3CH_2CH_2CN \xrightarrow{LiAlH_4} CH_3CH_2CH_2CH_2NH_2$$

(Another route that reaches four carbons earns the marks too: for example, a second Grignard and methanal step to butan-1-ol, then 1-bromobutane and a large excess of ammonia.)

iii. An aldehyde other than methanal and a Grignard reagent give a secondary alcohol (any route that works earns the marks):

$$CH_3CH_2MgBr + CH_3CHO \rightarrow CH_3CH_2CH(OMgBr)CH_3 \xrightarrow{H_2O} CH_3CH_2CH(OH)CH_3$$

MARKING SCHEME

- ✓ i. Bromoethane + alcoholic KCN gives propanenitrile.
- ✓ i. Hydrolysis with dilute acid gives propanoic acid.
- ✓ ii. Bromoethane + Mg in dry ether, then methanal and water, gives propan-1-ol.
- ✓ ii. Propan-1-ol to 1-bromopropane (PBr_3, or NaBr + conc. H_2SO_4).
- ✓ ii. KCN, then $LiAlH_4$ reduction of butanenitrile, gives butan-1-amine (another route that reaches four carbons earns these three marks).
- ✓ iii. Ethylmagnesium bromide + ethanal, then water, gives butan-2-ol.

b. **ANSWER** HA · 2

Tests: a flat intermediate attacked from either face gives a racemic product, here a C=O instead of a carbocation.

No, it is racemic. Butan-2-ol has a chiral carbon (C-2: H, OH, CH_3, C_2H_5), but it is made from ethanal's **flat** C=O carbon. The Grignard reagent's ethyl group can bond to either face of that flat carbon with equal chance, just as a nucleophile reaches either face of the flat carbocation in SN1, so the two enantiomers form in equal amounts. (Nothing chiral was there to favor one face: the starting materials are all achiral.)

MARKING SCHEME

- ✓ Racemic (optically inactive), although C-2 is chiral.
- ✓ The ethyl group adds to either face of the flat C=O equally, as a nucleophile does to a flat carbocation.

6 A clean chloride out of the flask

ANSWER A · 5

Tests: practical choices: a reagent chosen by the alcohol's class and its by-products; density, not being "organic", decides the layer.

i. **Phosphorus pentachloride.** Lucas reagent hardly reacts with a primary alcohol in the cold (it needs heating with a primary alcohol, and is quick only for tertiary ones). PCl_5 reacts in the cold: $CH_3CH_2CH_2CH_2OH + PCl_5 \rightarrow CH_3CH_2CH_2CH_2Cl + POCl_3 + HCl$. The HCl escapes as a gas; the $POCl_3$ (boiling point 106 °C) is separated by **distilling**: the chloride comes over first, at 78 °C.

ii. **Yes: Lucas reagent.** A tertiary alcohol reacts with it at once at room temperature, and the chloride, insoluble in the reagent, separates as a layer: there is no phosphorus by-product to distil off.

iii. **Today the upper layer**: 1-chlorobutane (0.89) is less dense than water. **For 1-bromobutane the lower one** (1.27). The bromides sink and this chloride floats: which layer is the product depends on its density, not on its being the organic one.

MARKING SCHEME

- ✓ PCl_5, since Lucas reagent hardly reacts with a primary alcohol in the cold.
- ✓ HCl escapes; distil the chloride (78 °C) away from $POCl_3$ (106 °C).
- ✓ For the tertiary alcohol, Lucas reagent: it reacts at once and leaves no phosphorus by-product.
- ✓ Today the upper layer (0.89 g/mL floats).
- ✓ For 1-bromobutane the lower layer (1.27 g/mL sinks).

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7 One order or two?

ANSWER HA · 3

Tests: what each mechanism's slow step contains, used to explain both orders at once.
In **both** mechanisms the slow step breaks the C–X bond: on its own in SN1, while the nucleophile arrives in SN2. A weaker, longer bond and a more stable halide ion make that easier either way, so **I > Br > Cl in both**. But alkyl groups on the carbon act on the two slow steps differently: in SN1 they **stabilize the carbocation** being formed (+I effect), so more of them is faster; in SN2 the nucleophile must reach the back of that carbon, and they **block the way** (steric hindrance), so more of them is slower.

MARKING SCHEME

- ✓ Both slow steps break the C–X bond, so the weaker bond and better leaving group (I) are faster in both.
- ✓ In SN1 alkyl groups stabilize the carbocation: 3° fastest.
- ✓ In SN2 alkyl groups hinder the backside attack: 1° (methyl) fastest.

Marks by level	Knowledge	Understanding	Application	Higher ability	Total
Marks	0	0	27	19	**46**

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