2023 JC2 H2 CHEMISTRY (9729)
ORGANIC CHEMISTRY
Topic 6: CARBONYL COMPOUNDS

Name: ____ Civics Group: _________

Students should be able to:

(a) describe the formation of aldehydes and ketones from, and their reduction to, primary and secondary alcohols respectively
(b) describe the mechanism of the nucleophilic addition reactions of hydrogen cyanide with aldehydes and ketones
(c) explain the differences in reactivity between carbonyl compounds and alkenes towards nucleophilic reagents, such as lithium aluminium hydride and hydrogen cyanide
(d) describe the use of 2,4-dinitrophenylhydrazine (2,4-DNPH) to detect the presence of carbonyl compounds
(e) deduce the nature (aldehyde or ketone) of an unknown carbonyl compound from the results of simple tests (*i.e.* Fehling's and Tollens' reagents; ease of oxidation)
(f) deduce the presence of a $CH_3CO–$ group in a carbonyl compound from its reaction with alkaline aqueous iodine to form tri-iodomethane

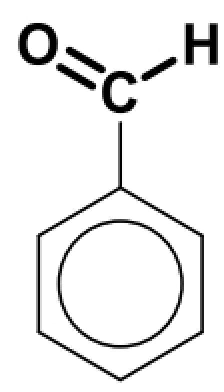
LECTURE CONTENT

REFERENCES:

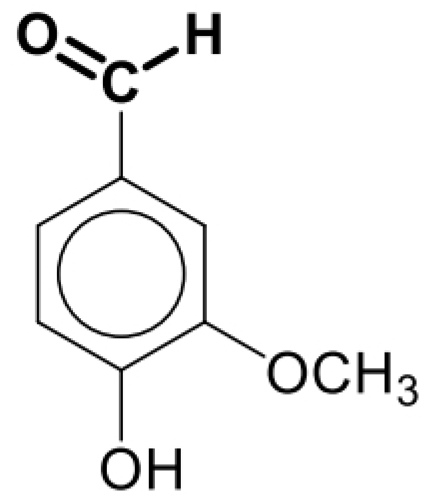
1. **Chemistry (for CIE AS & A Level)** by Peter Cann & Peter Hughes
2. **Understanding Advanced Organic and Analytical Chemistry: The Learner's Approach** by Chan Kim Seng and Jeanne Tan
3. **Understanding Chemistry - Organic Reaction Mechanisms**
   URL : http://www.chemguide.co.uk/mechanisms/nucadd/hen.html

1 Introduction to Carbonyl Compounds

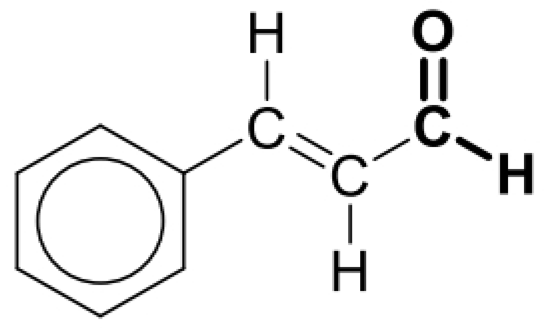
- **Natural Occurrence**
  Carbonyl compounds are prevalent in nature.
  They appear as natural fragrances and flavourings, and in other naturally-occurring compounds like vitamins, hormones and carbohydrates.



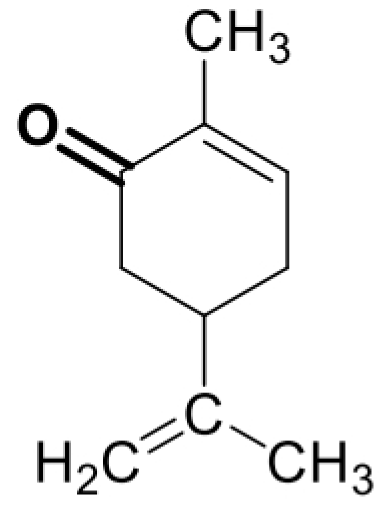
benzaldehyde
(almond-like odour)



vanillin
(vanilla-like odour)

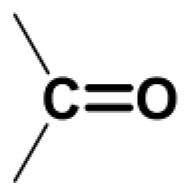


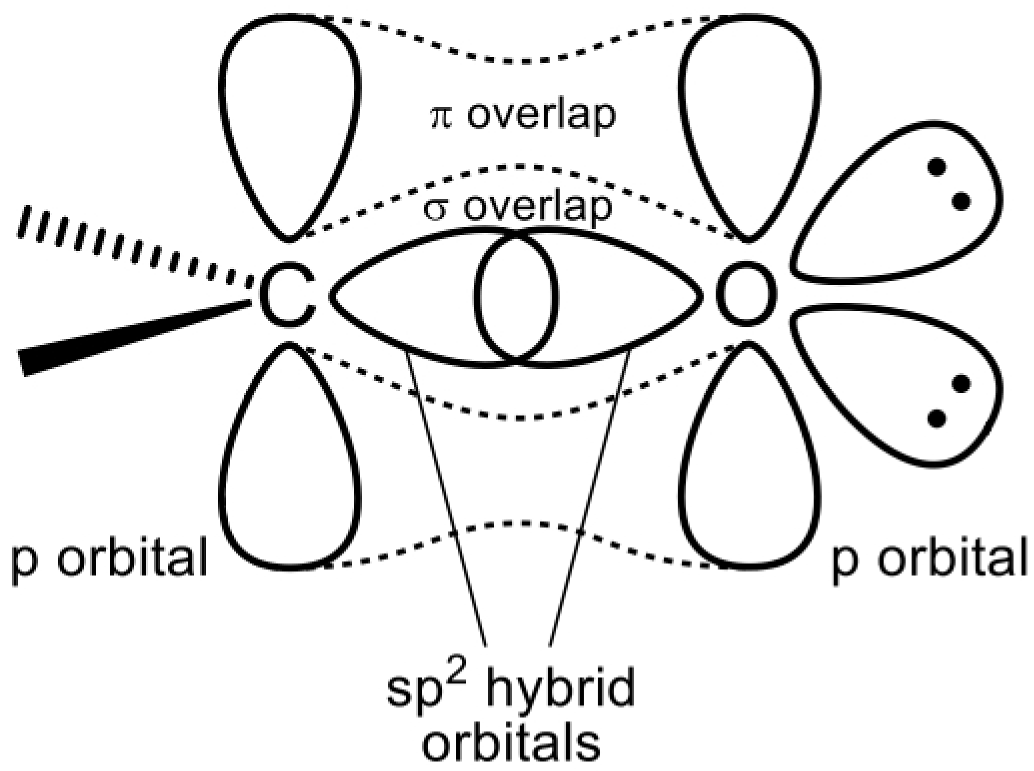
cinnamaldehyde
(cinnamon-like odour)



carvone
(spearmint)

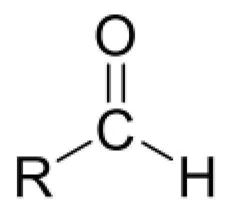
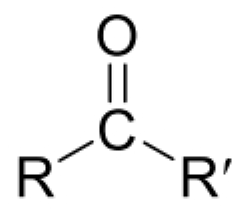
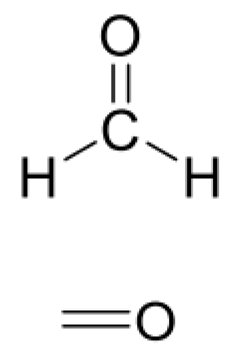
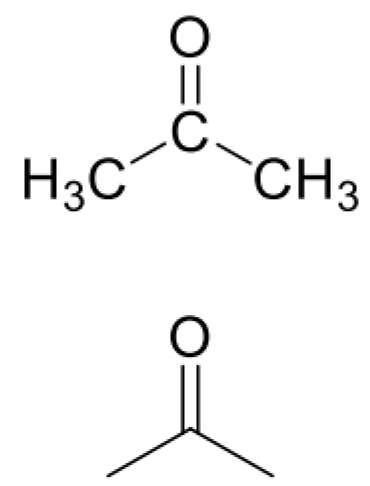
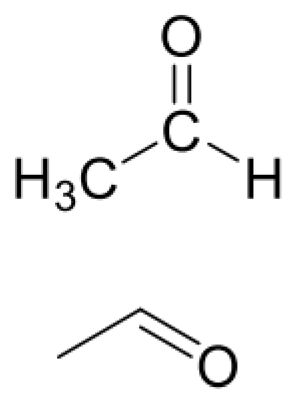
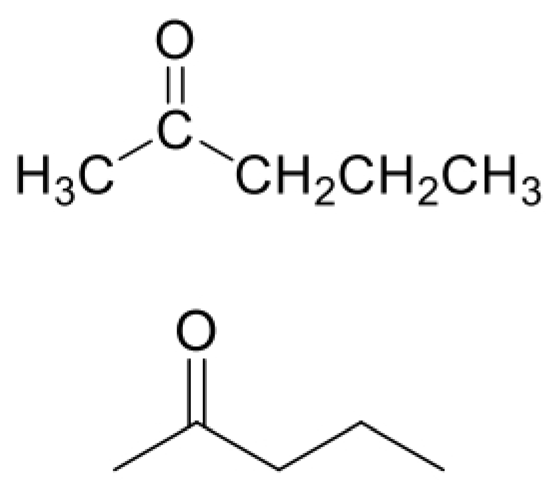
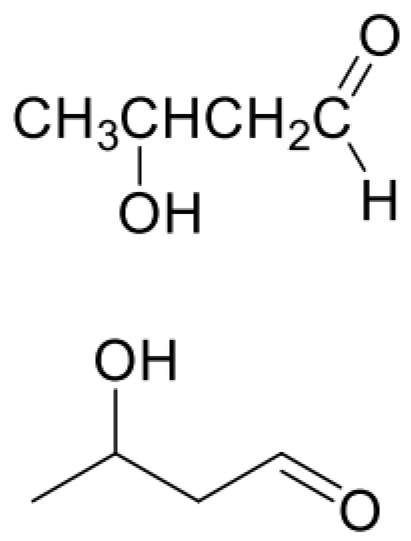
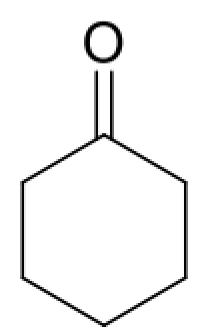
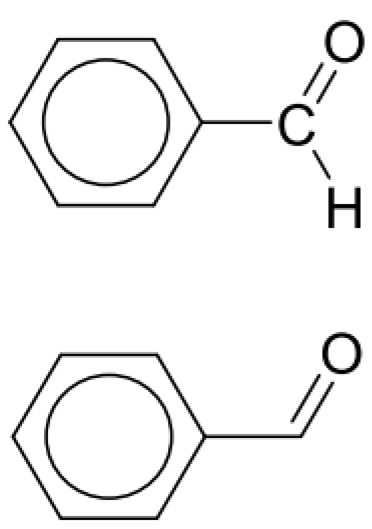
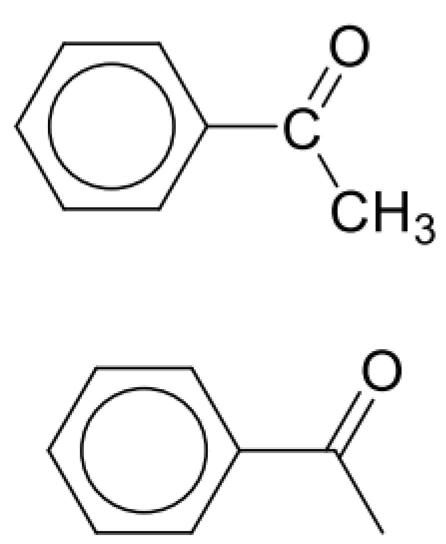
- **Carbonyl compounds** contain the carbonyl functional group.

Carbonyl functional group: 



- Carbonyl carbon is **<u>sp² hybridised</u>** and lies on the **same plane as the three atoms directly attached to it** (*i.e.* **<u>trigonal planar</u>** arrangement of atoms).
- The bond angle is approximately **<u>120°</u>**.

- Two types of carbonyl compounds: **Aldehydes** and **Ketones**

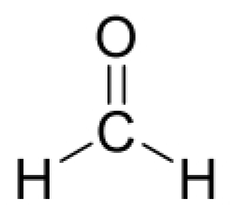
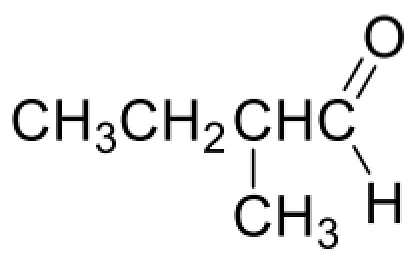
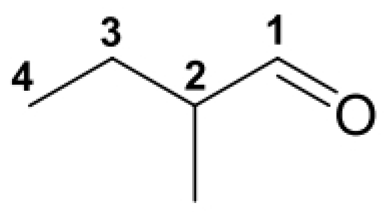
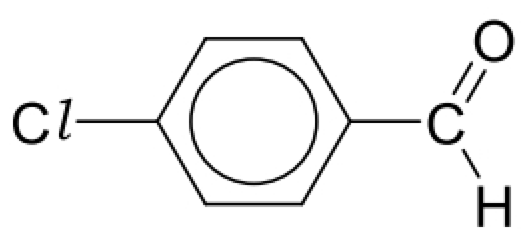
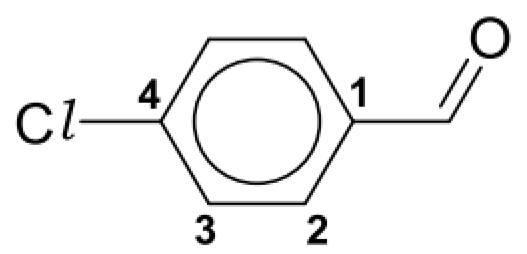
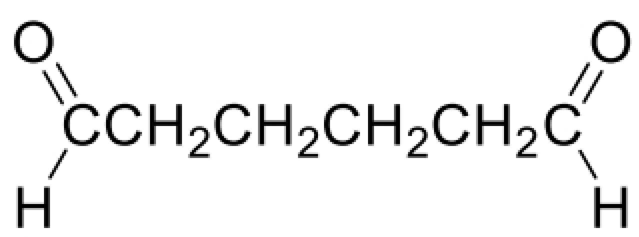
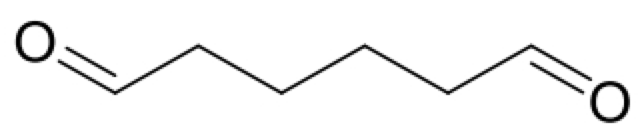
Aldehyde (**RCHO**) **(not RCOH!)**		**Ketone** (**RCOR′**)	
General Formula :  where R can be **H, alkyl or aryl** group		**General Formula** :  where R and R′ can be **alkyl or aryl** group	
Examples:		**Examples:**	
	methanal (acetaldehyde)		propanone
	ethanal		pentan-2-one
	3-hydroxybutanal		cyclohexanone
	benzenecarbaldehyde (benzaldehyde)		phenylethanone (acetophenone)

Saturated aliphatic aldehydes and ketones have the same general formula $\mathbf{C_nH_{2n}O}$, where ***n*** is the number of C atoms in the compound.

2 Nomenclature

2.1 Aldehydes

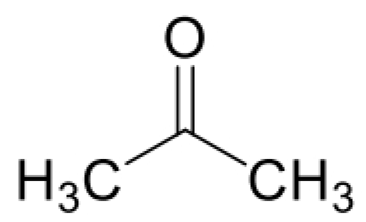
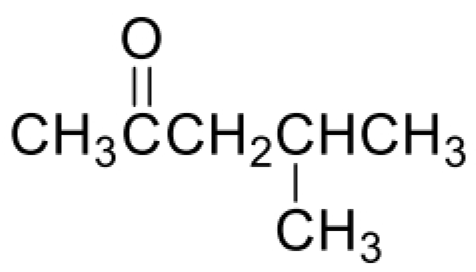
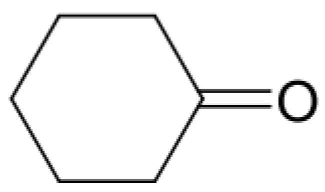
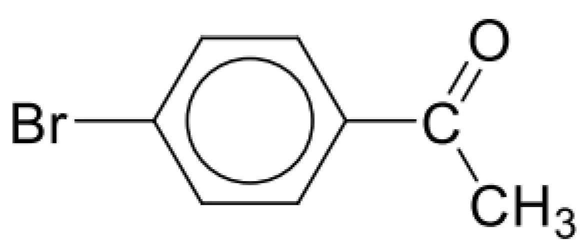
- Named by **replacing the terminal '*e*'** from the corresponding alkane **with '*al*'**,
- **Longest chain carrying -CHO** group is the **parent** structure,
- The **carbonyl carbon** is always **considered as C-1**,
- **Aromatic** aldehyde: **carbonyl carbon is directly bonded to benzene** ring.

Examples:	
Structural formula	**IUPAC Name**
	methanal
 	2-methylbutanal
 	4-chlorobenzenecarbaldehyde (4-chlorobenzaldehyde)
 	hexanedial

2.2 Ketones

- Named by **replacing the terminal '*e*'** from the corresponding alkane **with '*one*'**,
- **Longest chain carrying the C=O** group is the **parent** chain,
- **Positions** of various groups are **indicated by number**, with the **carbonyl carbon being given the lowest possible number**,
- If a ketone is to be **named as a prefix** (*i.e.* substituent), then ***-oxo-*** is used,
- **Aromatic** ketone: **carbonyl carbon <u>directly</u> bonded to benzene ring**.

Examples:

Structural formula	**IUPAC Name**
 Try to draw the skeletal structure.	propanone
 Try to draw the skeletal structure.	4-methylpentan-2-one
	cyclohexanone
 Try to draw the skeletal structure.	4-bromophenylethanone

Self Check 2A

Draw all the structural isomers of $C_5H_{10}O$, each containing the carbonyl functional group.

[*Hint: Aldehydes and ketones are isomeric (constitutional isomers) with one another.*]

3 Physical Properties

3.1 Boiling points

compound	structural formula	M_r	b.p. / °C	predominant intermolecular forces
butane	$CH_3CH_2CH_2CH_3$	58	–0.5	instantaneous dipole–induced dipole
propanal	CH_3CH_2**CHO**	58	49	permanent dipole–permanent dipole
propanone	CH_3**CO**CH_3	58	56	permanent dipole–permanent dipole
propan-1-ol	$CH_3CH_2CH_2$**OH**	60	97	hydrogen bonds
propanoic acid	CH_3CH_2**COOH**	60	118	hydrogen bonds

- Boiling points of carbonyl compounds are **higher** than that of the **corresponding alkanes or alkenes having similar M_r**.

  Explanation:

  More energy is needed to overcome the **stronger permanent dipole–permanent dipole interactions between carbonyl molecules** than the **weaker instantaneous dipole-induced dipole interactions between alkane molecules** (or **alkenes**).

- Boiling points of carbonyl compounds are **lower** than that of the **corresponding alcohols or carboxylic acids** having **similar M_r**.

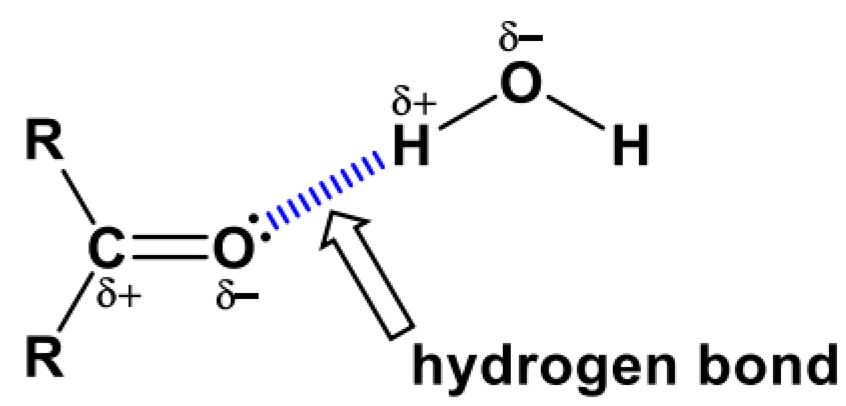
  Explanation:

  Less energy is needed to overcome the **weaker permanent dipole–permanent dipole interactions between carbonyl molecules** than the **stronger hydrogen bonds between alcohols molecules** (or **carboxylic acids**).

3.2 Solubility

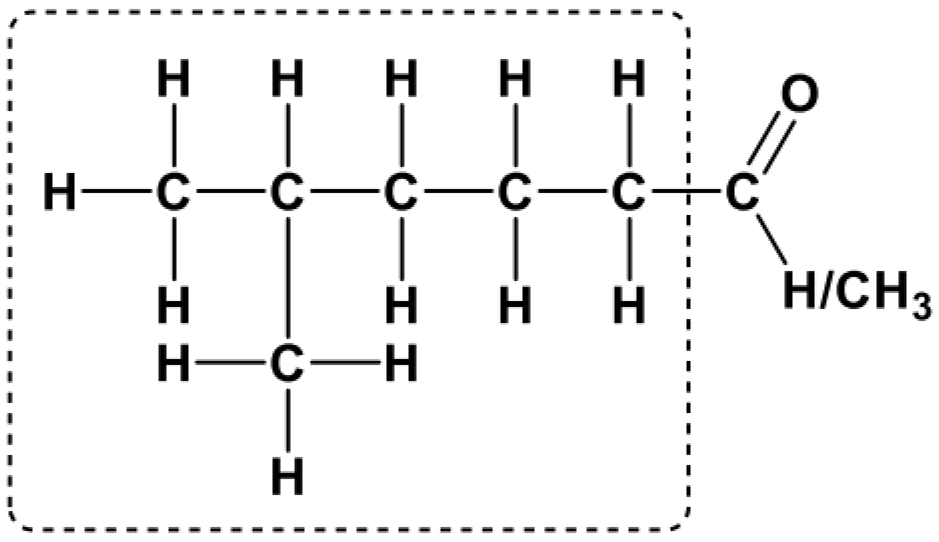
- Aldehydes and ketones with **smaller number of C atoms** such as methanal, ethanal, and propanone are **completely miscible** with water.

  Reason: Aldehydes and ketones can **form hydrogen bonds with water molecules**.



- **Solubility of aldehydes/ketones in water decreases** for **aldehydes/ketones** with **larger number of C atoms**.

  Reason: The **larger non-polar alkyl/aryl group makes the molecule less soluble.** The **permanent dipole-induced dipole interactions** between the hydrophobic group and water molecules **do not release sufficient amount of energy** to overcome the strong **hydrogen bonds** between the water molecules. In addition, the larger alkyl group also **hinders the formation of hydrogen bonds between the carbonyl functional group and water molecules**.



Large non-polar alkyl group hinders formation of hydrogen bond

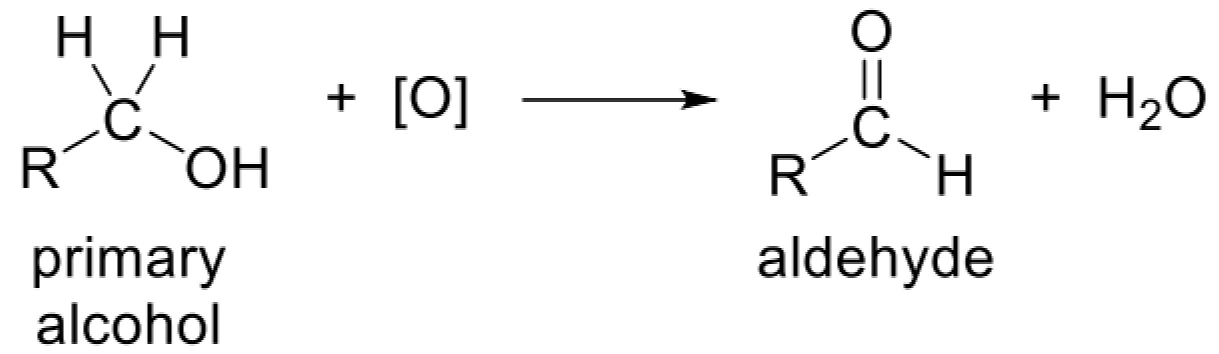
At the end of these sections, you should know that:

- The carbonyl carbon in the aldehyde and ketone functional groups is sp^2 hybridised, trigonal planar shape with bond angle of 120°.
- The lone pair of electrons on the C=O group can form hydrogen bonds with water molecules. In general, aldehydes and ketones of lower molecular weight are soluble in water.
- However, aldehydes and ketones of higher molecular weight are insoluble in water due to the presence of large hydrophobic alkyl group. Hence, they are unable form favourable interactions with water molecules.

LO (a) describe the formation of aldehydes and ketones from, and their reduction to, primary and secondary alcohols respectively

4 Preparation of Carbonyl Compounds

4.1 Oxidation of Primary Alcohols to form Aldehydes

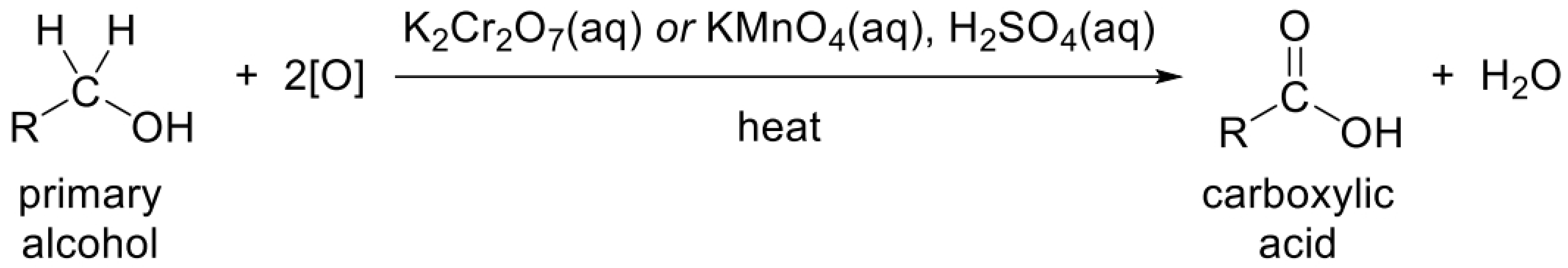


R = alkyl, aryl

Reagents and conditions: $K_2Cr_2O_7$(aq), H_2SO_4(aq), immediate distil
Observations: Orange $K_2Cr_2O_7$ solution turns green
Type of reaction: Oxidation

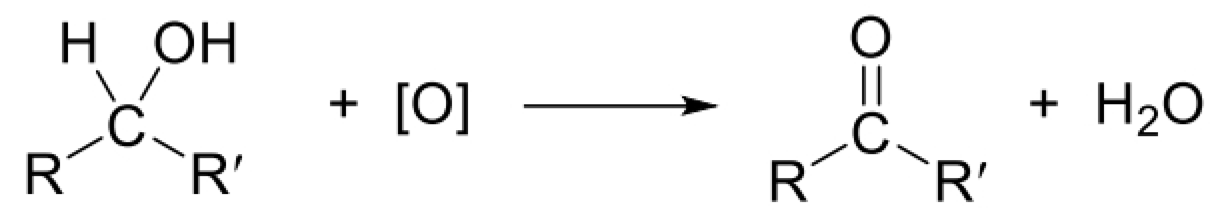
Note:

Primary alcohols will be ***oxidised to carboxylic acid when heated without immediate distillation***.



$KMnO_4$, a **stronger** oxidising agent than $K_2Cr_2O_7$, will oxidise primary alcohol to carboxylic acid. Hence $KMnO_4$ cannot be used to make an aldehyde.

4.2 Oxidation of Secondary Alcohols to form Ketones



secondary alcohol → ketone

R, R′ = alkyl, aryl

Reagents and conditions: $K_2Cr_2O_7$(aq), H_2SO_4(aq), heat **OR**
$KMnO_4$(aq), H_2SO_4(aq), heat

Observations: Orange $K_2Cr_2O_7$ solution turns green **OR**
Purple $KMnO_4$ solution is decolourised.

Type of reaction: Oxidation

Note:

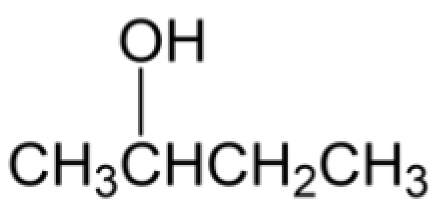
Tertiary alcohols are generally **resistant to oxidation** by acidified $KMnO_4$(aq) or $K_2Cr_2O_7$(aq) for A-level.

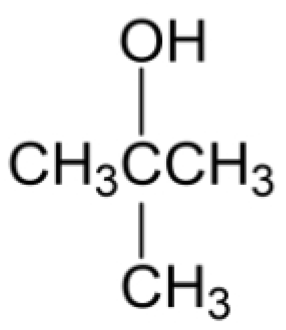
Self-Check 4A

Draw the structures of the products formed and balance the equation using [O].

(a) $CH_3CH_2CH_2CH_2OH$ —— $K_2Cr_2O_7$(aq), H_2SO_4(aq) / immediate distill ——→

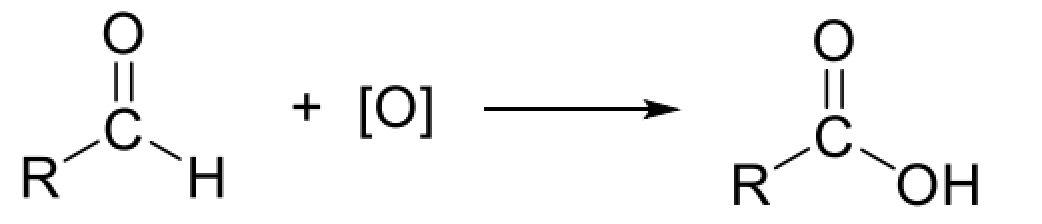
(b) $CH_3CH_2CH_2CH_2OH$ —— $K_2Cr_2O_7$(aq) / $KMnO_4$(aq), H_2SO_4(aq) / heat ——→

(c)  —— $K_2Cr_2O_7$(aq) / $KMnO_4$(aq), H_2SO_4(aq) / heat ——→

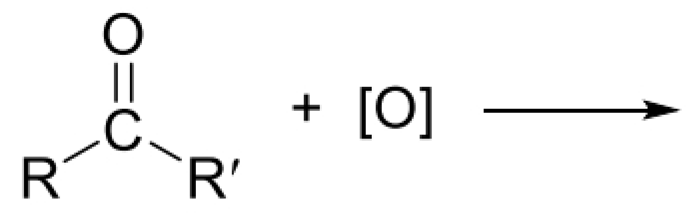
(d)  —— $K_2Cr_2O_7$(aq) / $KMnO_4$(aq), H_2SO_4(aq) / heat ——→

5 Reactions of Carbonyl Compounds

5.1 Oxidation



aldehyde — carboxylic acid



no reaction (inert to oxidation)

ketone

R, R′ = alkyl, aryl

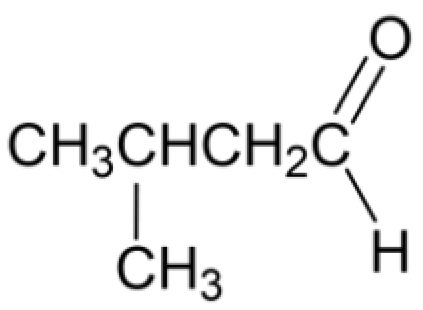
Reagents and conditions: $K_2Cr_2O_7$(aq), H_2SO_4(aq), heat **OR** $KMnO_4$(aq), H_2SO_4(aq), heat

Observations: Orange $K_2Cr_2O_7$ solution turns green **OR** Purple $KMnO_4$ solution is decolourised.

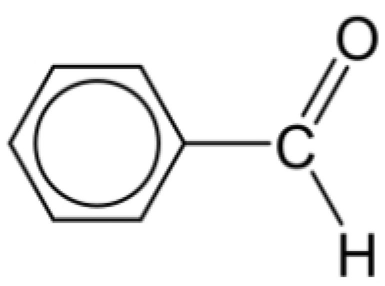
Type of reaction: Oxidation

Example 5A

Draw the structures of the products formed and balance the equation using [O].

(a) 

$K_2Cr_2O_7$(aq) / $KMnO_4$(aq), H_2SO_4(aq) ⟶ heat

(b) 

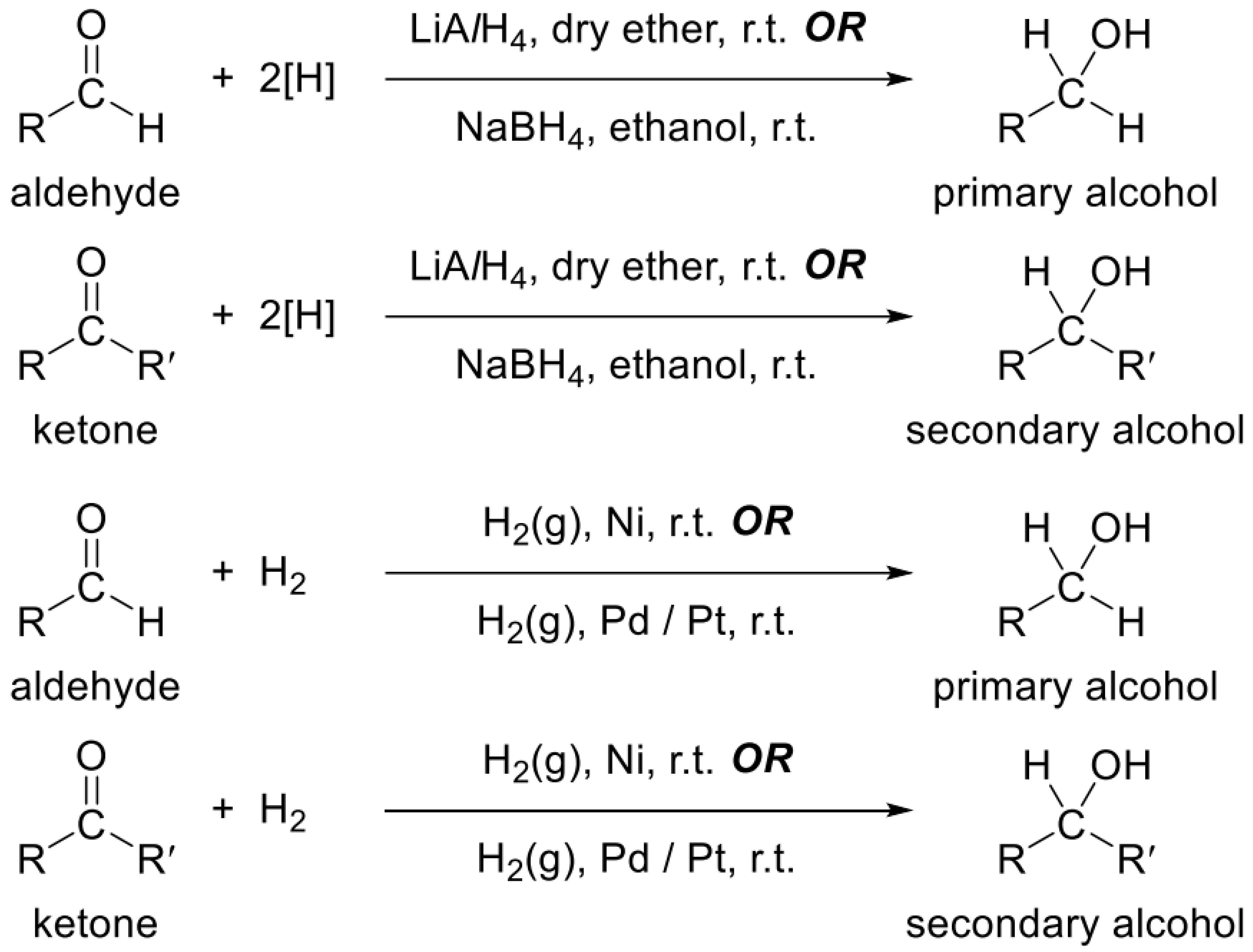
$K_2Cr_2O_7$(aq) / $KMnO_4$(aq), H_2SO_4(aq) ⟶ heat

(c) $CH_3COCH_2CH_3$

$K_2Cr_2O_7$(aq) / $KMnO_4$(aq), H_2SO_4(aq) ⟶ heat

LO (a) describe the formation of aldehydes and ketones from, and their reduction to, primary and secondary alcohols respectively

5.2 Reduction



R, R′ = alkyl, aryl

Reagents and conditions: $LiAlH_4$, dry ether, r.t. **OR**
$NaBH_4$, ethanol, r.t. **OR**
H_2(g), Ni, r.t. **OR**
H_2(g), Pd or Pt, r.t.

Type of reaction: Reduction

<u>Note</u>:

- $LiAlH_4$ must be used in **<u>dry</u>** conditions as it ***reacts violently with water***:

$$LiAlH_4 + 4H_2O \rightarrow LiOH + Al(OH)_3 + 4H_2$$

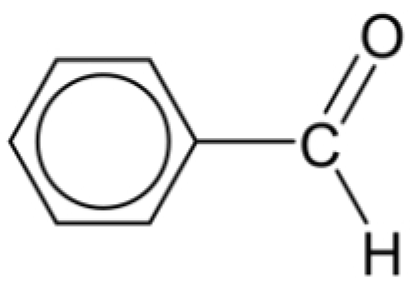
- $LiAlH_4$ is also ***thermally unstable*** above 120 ºC and hence, **<u>no heating</u>**.

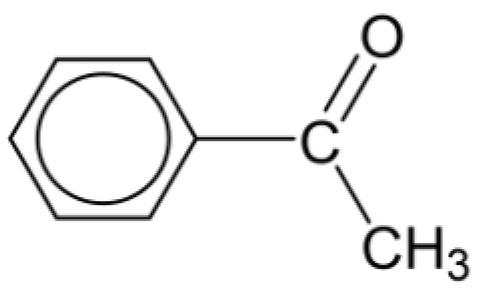
Example 5B

Draw the structures of the products formed and balance the equation using [H] or H_2.

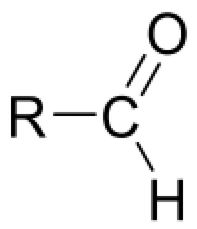
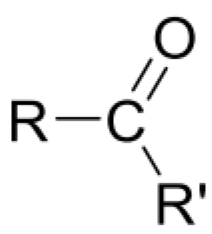
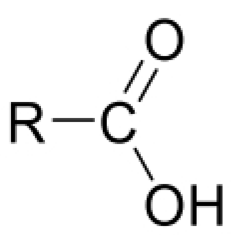
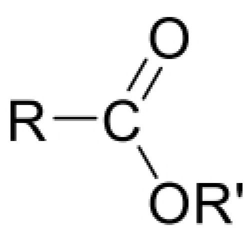
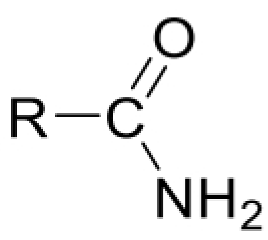
(a) CH_3CH_2CHO $\xrightarrow[\text{NaBH}_4\text{, ethanol, r.t.}]{\text{LiA}l\text{H}_4\text{, dry ether, r.t. } \textbf{\textit{OR}}}$

(b) CH_3COCH_3 $\xrightarrow[\text{H}_2\text{(g), Pd / Pt, r.t.}]{\text{H}_2\text{(g), Ni, r.t. } \textbf{\textit{OR}}}$

(c)  $\xrightarrow[\text{NaBH}_4\text{, ethanol, r.t.}]{\text{LiA}l\text{H}_4\text{, dry ether, r.t. } \textbf{\textit{OR}}}$

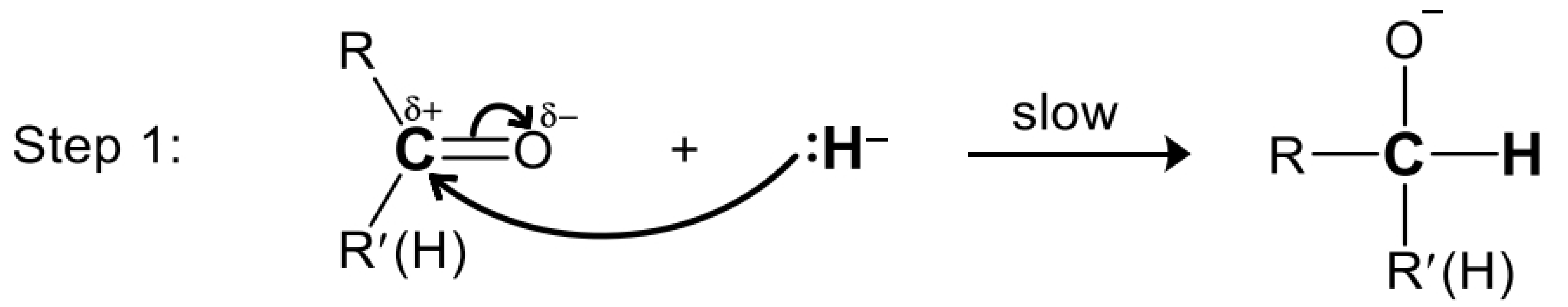
(d)  $\xrightarrow[\text{NaBH}_4\text{, ethanol, r.t.}]{\text{LiA}l\text{H}_4\text{, dry ether, r.t. } \textbf{\textit{OR}}}$

SUMMARY OF PROPERTIES OF REDUCING AGENTS

functional groups	**ability to be reduced by**		
	H_2, Ni, r.t.	**LiAlH$_4$, dry ether**	**NaBH$_4$, ethanol**
C=C, C≡C	✓	✗	✗
nitriles, R–C≡N	✓	✓	✗
aldehydes, 	✓	✓	✓
ketones, 	✓	✓	✓
carboxylic acid, 	✗	✓	✗
ester, 	✗	✓	✗
amide, 	✗	✓	✗

Note:

- **LiAlH$_4$ and NaBH$_4$ cannot reduce alkenes and alkynes** (C≡C).
  Both **LiAlH$_4$ and NaBH$_4$ provide :H$^-$ nucleophiles which attack electron-deficient C atom** of the reactant molecule. The C=C bond of alkenes and C≡C bond of alkynes are electron-rich but non-polar and hence will not react with these reagents.
  (See Page 27 for the simplified version of the mechanism!)



- **NaBH$_4$**, a weaker reducing agent than LiAlH$_4$, can **only reduce aldehydes and ketones**.
- **Why LiAlH$_4$ is a stronger reducing agent than NaBH$_4$?**

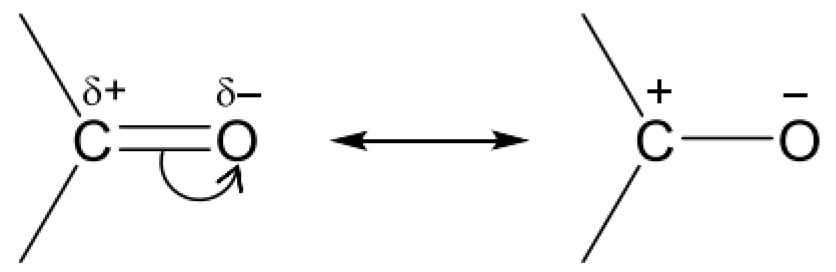
As Al is more electropositive than B, the $\overset{\delta+}{\text{A}l}-\overset{\delta-}{\text{H}}$ bond is more polar and the H in AlH_4^- will have a larger partial negative charge (δ–) and hence **more nucleophilic** than that in BH_4^-.

Recall: the more electronegative an atom, the less likely it will share or give up electrons.

At the end of these sections, you should know that:

- Aldehydes can be prepared via oxidation from 1° alcohol using "$K_2Cr_2O_7$, H_2SO_4, heat with **immediate distillation**" as oxidising agent.
- Aldehyde can be prepared via oxidation to carboxylic acid using "$K_2Cr_2O_7$, H_2SO_4, heat or $KMnO_4$, H_2SO_4, heat" as oxidising agent.
- Ketones can be prepared via oxidation from 2° alcohol using "$K_2Cr_2O_7$, H_2SO_4, heat or $KMnO_4$, H_2SO_4, heat" as oxidising agent.
- Aldehydes and ketones can be reduced to the respective 1° and 2° alcohols using the following reducing agengs: "LiA1H$_4$ in dry ether, r.t." or "NaBH$_4$ in ethanol, r.t." or "H$_2$ with Ni/Pt catalyst".
- "LiA1H$_4$ in dry ether, r.t." is a stronger reducing agent than "NaBH$_4$ in ethanol, r.t." because only "LiA1H$_4$ in dry ether, r.t." can reduce carboxylic acids.

5.3 Nucleophilic Addition Reactions



- Due to the high electronegative of the O atom, and contribution of the dipolar resonance structure, the **C=O** bond of the carbonyl group is **highly polar**. The **partially positive carbonyl C atom (<u>$C^{\delta+}$</u>)** acts as an **<u>electron-deficient</u> site**, which will be **<u>attacked by a nucleophile</u>**.
- Since the C of C=O is **<u>unsaturated</u>**, it can undergo **<u>addition reaction</u>** readily.
  Hence, carbonyl compounds (*i.e.* aldehydes & ketones) undergo **nucleophilic addition**.

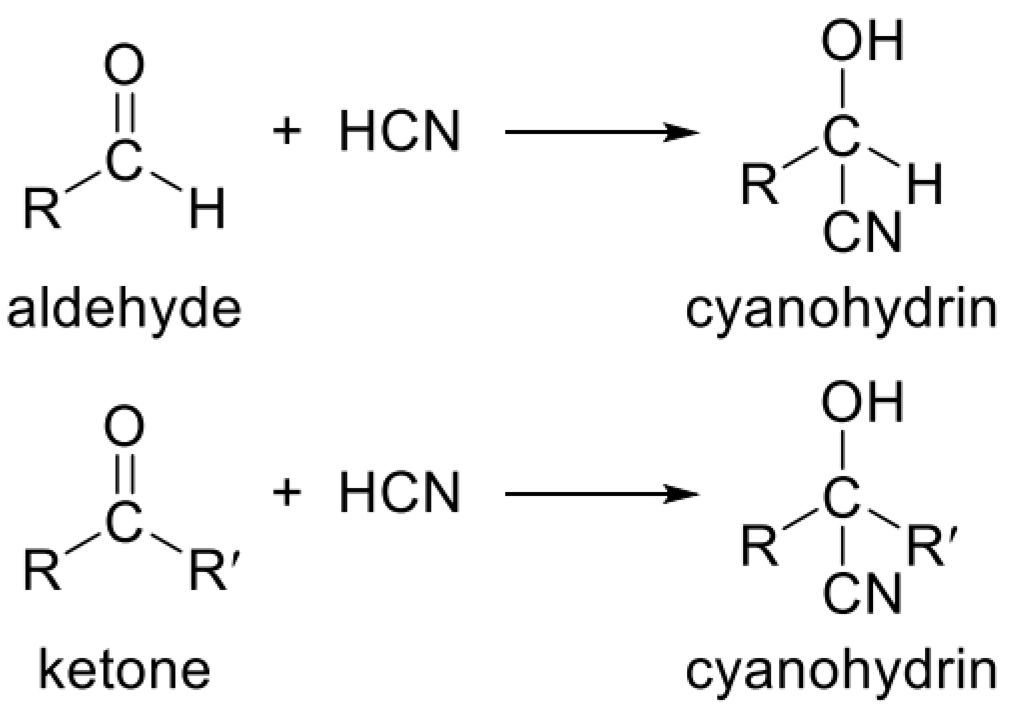
LO (c) explain the differences in reactivity between carbonyl compounds and alkenes towards nucleophilic reagents, such as lithium aluminium hydride and hydrogen cyanide

5.3.1 Differences in Reactivity between Carbonyl Compounds and Alkenes towards Nucleophilic Reagents

Although both alkenes (C=C) and carbonyl compounds (C=O) are unsaturated, they behave differently towards nucleophilic reagents, such as $LiAlH_4$ and HCN.

Carbonyl Compounds	Alkenes
The **<u>carbonyl carbon</u>** is **electron deficient** as it is **bonded to** an **electronegative oxygen atom**. Hence the carbonyl carbon is more susceptible to **nucleophilic attack** by nucleophilic reagents.	The **C=C of the alkene is electron-rich** (there is no electron-deficient C), hence it is **not** susceptible to **nucleophilic attack**.

5.3.2 Nucleophilic Addition Reaction with Hydrogen Cyanide



R, R′ = alkyl, aryl

Reagents and conditions: HCN, trace amount of NaCN **OR**
HCN, trace amount of NaOH
Cold

Type of reaction: Nucleophilic Addition

<u>Note</u>:

- As HCN is a toxic gas, it is usually generated *in situ* by reacting NaCN (*or* KCN) with dilute H_2SO_4(aq).

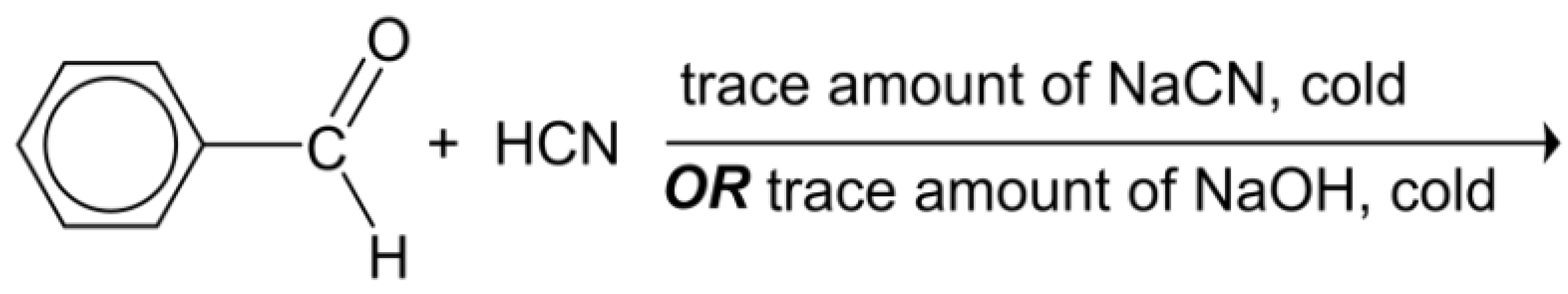
$$2NaCN + H_2SO_4 \rightarrow 2HCN + Na_2SO_4$$

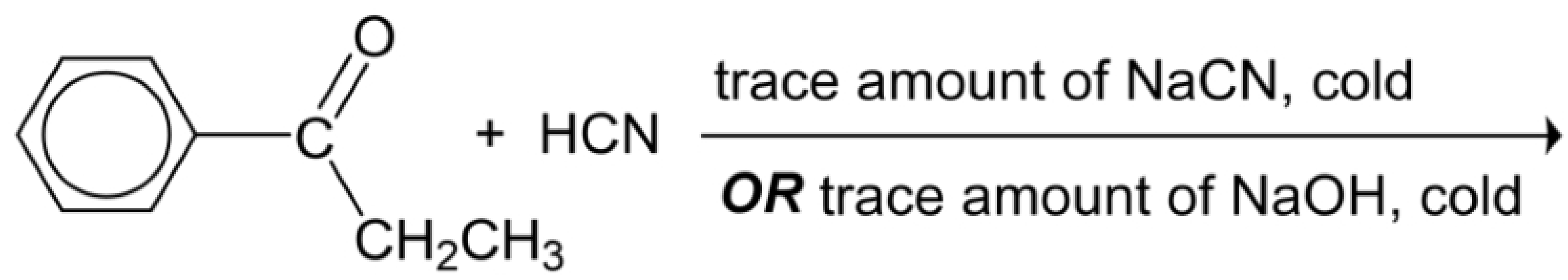
The pH of the solution is adjusted to about 4–5 to ensure a reasonable rate of reaction. The *solution will contain* ***HCN and some free CN^- ions*** which are important for the mechanism.

- HCN is a volatile gas (b.p. 26 ºC), there should be no heating to prevent the poisonous HCN from escaping into the environment. **Hence, the cold condition is needed.**

Self Check 5A

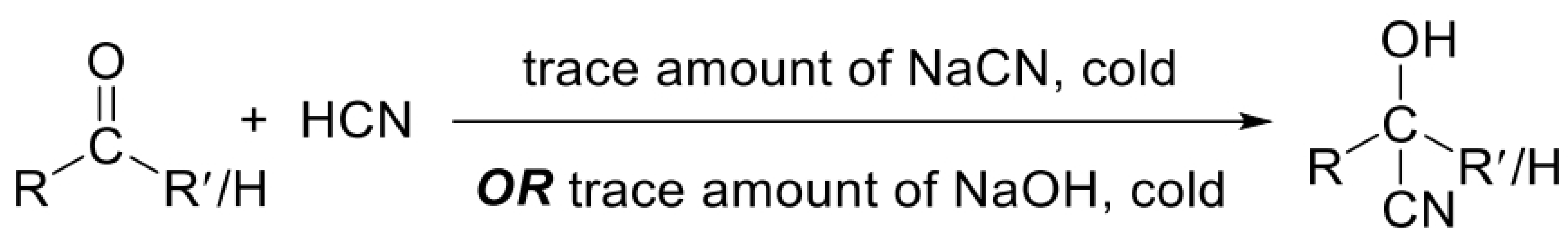
Predict the organic products of the following reactions.

(a) 

(b) 

LO (b)	describe the mechanism of the nucleophilic addition reactions of hydrogen cyanide with aldehydes and ketones

5.3.3 Nucleophilic Addition Mechanism with Hydrogen Cyanide

Overall equation: 

<u>Nucleophilic Addition Mechanism</u>

Generation of nucleophile

HCN is a <u>weak acid</u> (K_a = 5 × 10^{-10} mol dm^{-3}) and only <u>dissociates partially</u> to give CN^-.

$$HCN\ (aq) \rightleftharpoons H^+\ (aq) + CN^-\ (aq)$$

The concentration of CN^- has to be increased without totally removing all the HCN in the system. There are two ways to do this:

(1) Add a small amount of strong base such as NaOH(aq) and KOH(aq).

- $HCN + OH^- \rightarrow H_2O + CN^-$

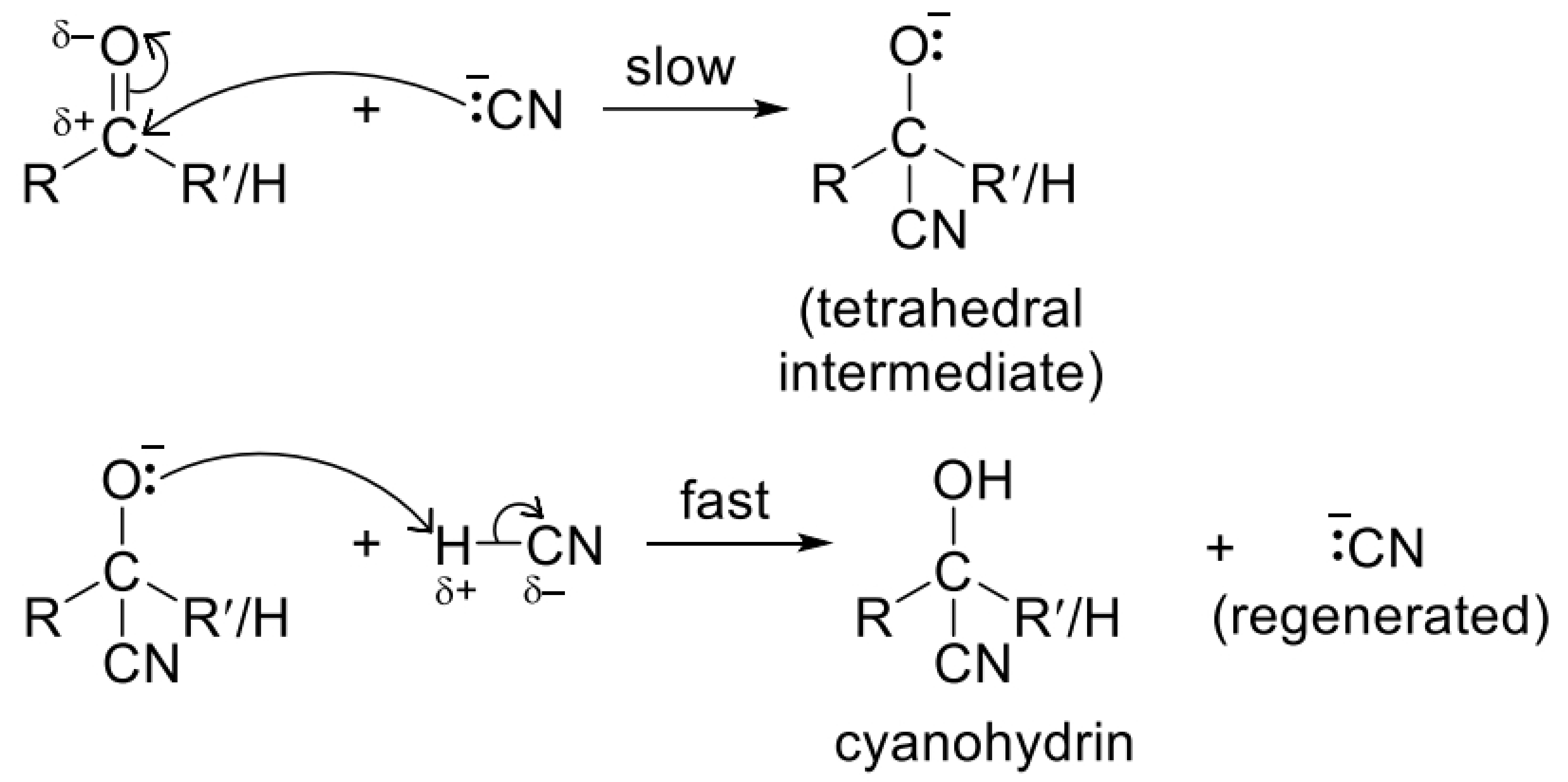
(2) Add a strong electrolyte containing CN^- such as NaCN(aq) and KCN(aq).
The complete ionisation of the electrolyte provides sufficient [CN^-] to start off the reaction.

- $NaCN \rightarrow Na^+ + CN^-$

Nucleophilic addition to form cyanohydrin in ***two steps***:

step 1:

step 2:



rate = *k*[carbonyl][CN⁻]

step 1: Attack by CN^- nucleophile (Lewis base) on the electron-deficient carbonyl carbon ($C^{\delta+}$ is a Lewis acid). The π electron pair of the carbon−oxygen bond shifts to the carbonyl oxygen, and this leads to the formation of a tetrahedral intermediate carrying a negative charge. This is the slow (rate-determining) step.

step 2: The tetrahedral intermediate undergoes ***protonation with HCN*** to yield the cyanohydrin. This is the fast step.

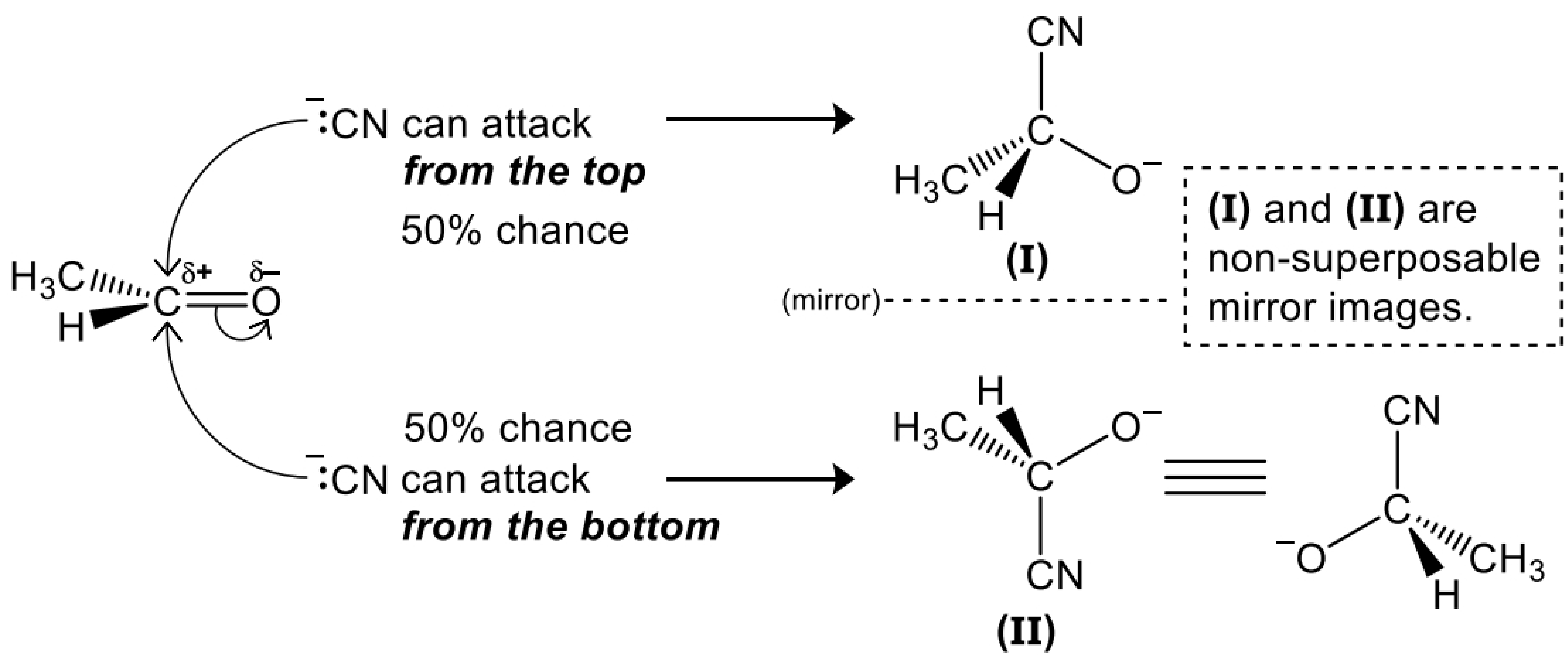
Important Notes for Nucleophilic Addition of HCN with Aldehydes and Ketones:

1. What is the role of HCN?

- **HCN acts as a Brønsted-Lowry acid (or proton donor) or a Lewis acid in Step 2** of the mechanism, protonating the intermediate anion.

2. Why is racemic mixture produced when an aldehyde or an *unsymmetrical* ketone undergo nucleophilic addition with HCN?

- There is an **equal probability of CN^- nucleophile to attack either side of the trigonal planar C of >C=O** group, producing a **racemic mixture** (*i.e.* 50:50 proportion of each enantiomer).



3. Suggest why cold condition is needed?

- The temperature cannot be too high so as to prevent the **poisonous HCN gas from escaping to the environment** as the boiling point of HCN is 26 ºC.
- The temperature cannot be too low so as to ensure rate of reaction is reasonably high.

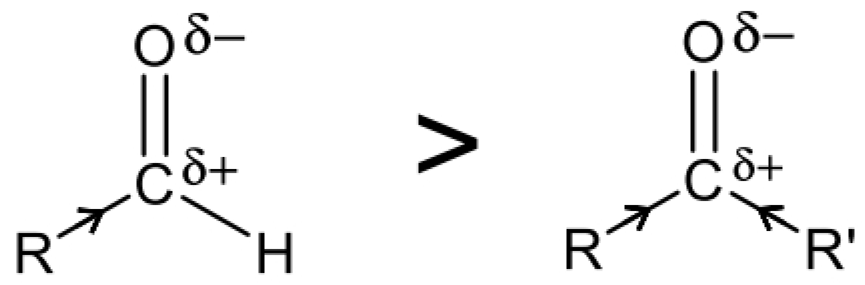
4. Why do aldehydes undergo nucleophilic addition *more rapidly* than ketones?

Explanation:

(a) **Electronic factor**:

Ketone has **one more electron-donating alkyl group**, which makes the **carbonyl carbon in ketones less electron-deficient**.

Reactivity of :



2 electron-donating alkyl groups
⟹ carbonyl C on ketone is less electron-deficient.

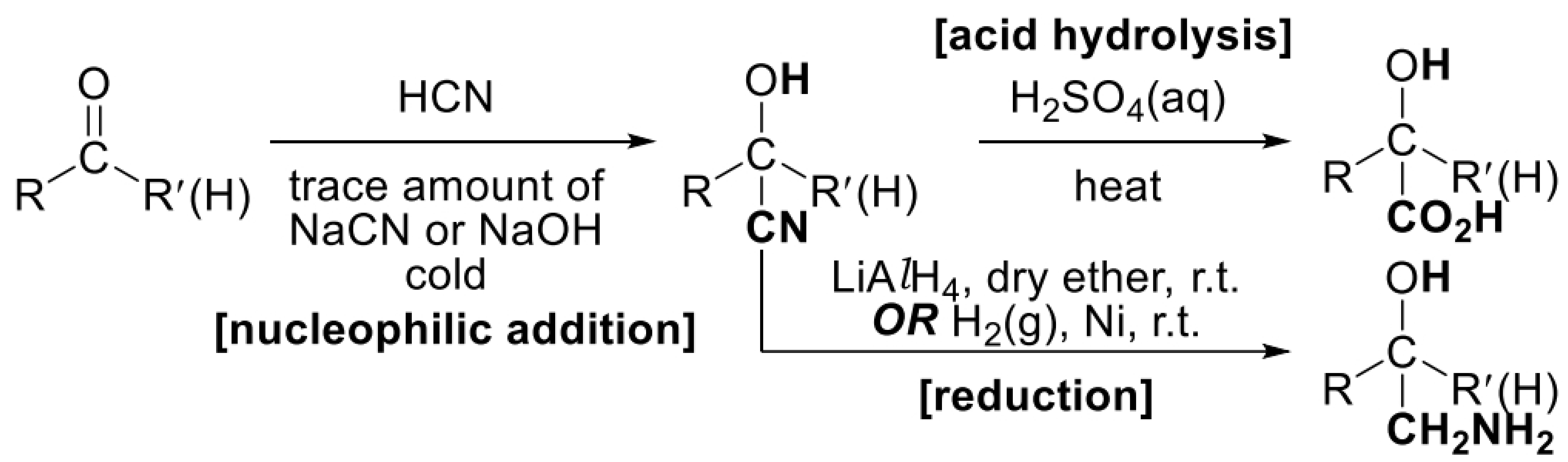
(b) **Steric factor**:

Ketone has **one more bulky alkyl/aryl group** attached to the carbonyl carbon. This **hinders the approach of nucleophiles** on the carbonyl carbon of ketones.

Hence, aldehydes undergo nucleophilic addition more readily/rapidly than ketones.

5. Why is the nucleophilic addition with HCN useful in organic synthesis?

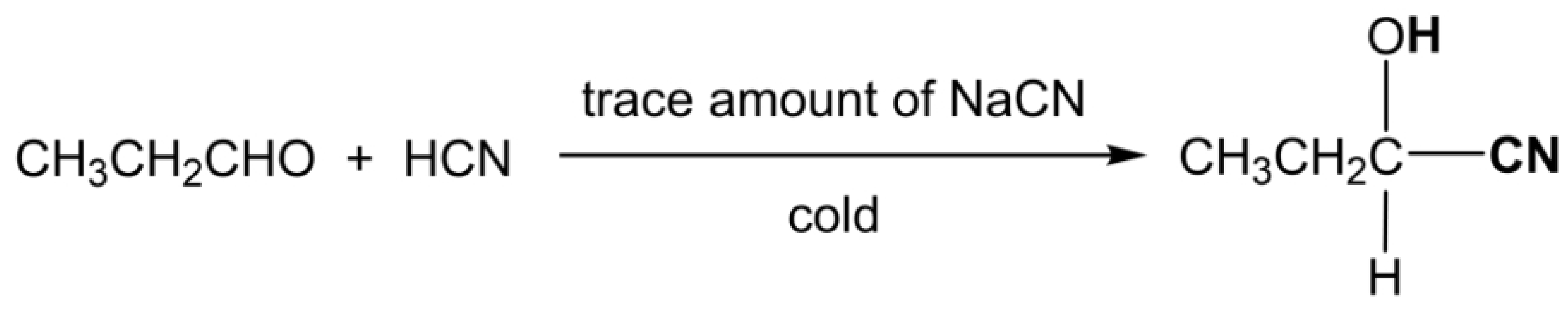
- The reaction of carbonyl compound with HCN involves the formation of C–C bond. Hence, this reaction **increases the number of carbon atoms in the molecule by one** (*i.e.* a ***step-up reaction***).
- **Cyanohydrins are useful organic intermediates**. They can be
  (a) ***hydrolysed*** to give ***2-hydroxycarboxylic acids*** **(–OH and –COOH)** (using dilute acid, heat); **(acid hydrolysis)**
  (b) ***reduced*** to give ***primary amines*** **(–OH and $-CH_2NH_2$)** (using $LiAlH_4$, dry ether *or* H_2(g), Ni, heat)



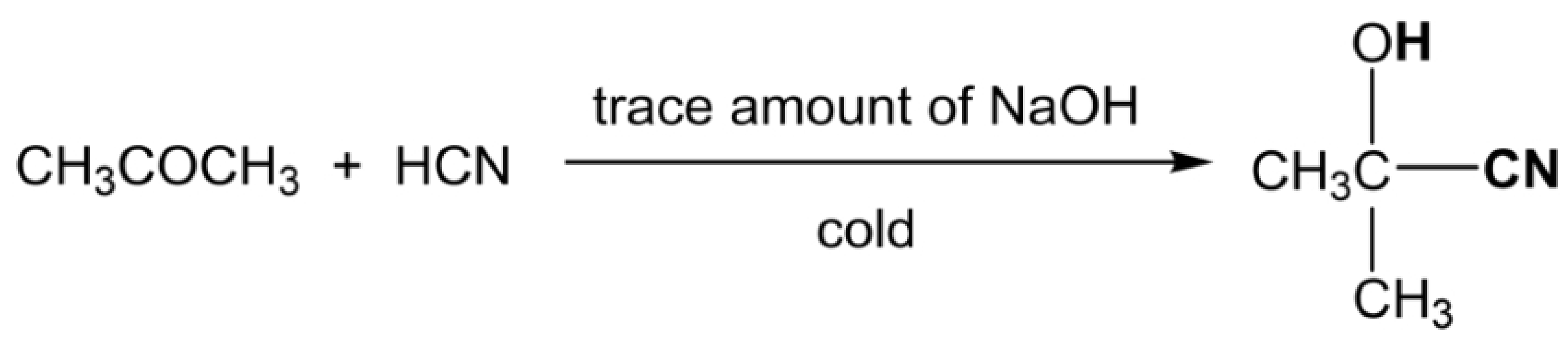
Self Check 5B

Predict the organic product and outline the mechanism of the reaction involved.

(a)



(b)



At the end of these sections, you should know that:

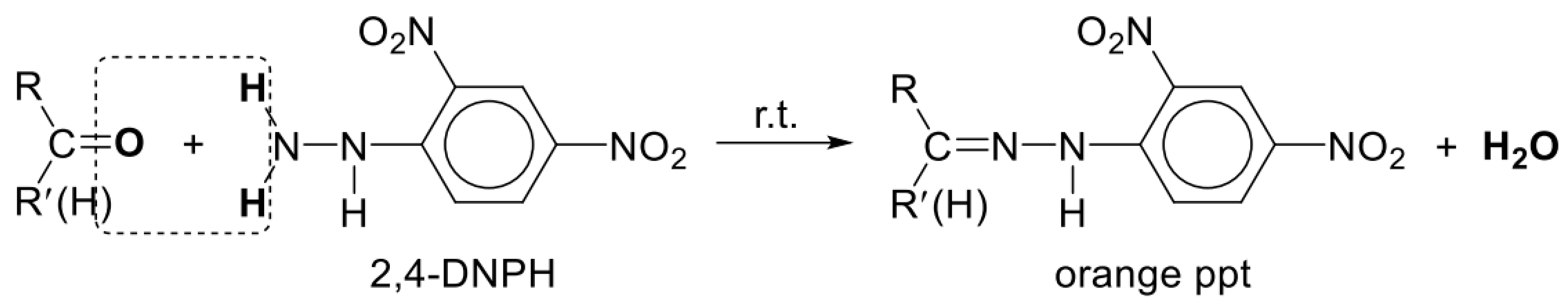
- Aldehydes are more susceptible to nucleophilic addition than ketones because the carbonyl carbon of aldehydes are more electron-deficient and experiences less steric hindrance when undergoing nucleophilic attack.
- A racemic mixture can result from the nucleophilic addition of an aldehyde or an asymmetrical ketone.

6 Distinguishing Tests for Carbonyl Compounds

LO (d) describe the use of 2,4-dinitrophenylhydrazine (2,4-DNPH) to detect the presence of carbonyl compounds

6.1 Reaction with 2,4-dinitrophenylhydrazine (2,4-DNPH)

❖ **Identification Test for Carbonyl Compounds (Aldehydes & Ketones)**



Reagents and conditions: 2,4-dinitrophenylhydrazine (2,4-DNPH), r.t.
Observations: Orange ppt.
Type of reaction: Condensation (addition followed by elimination)

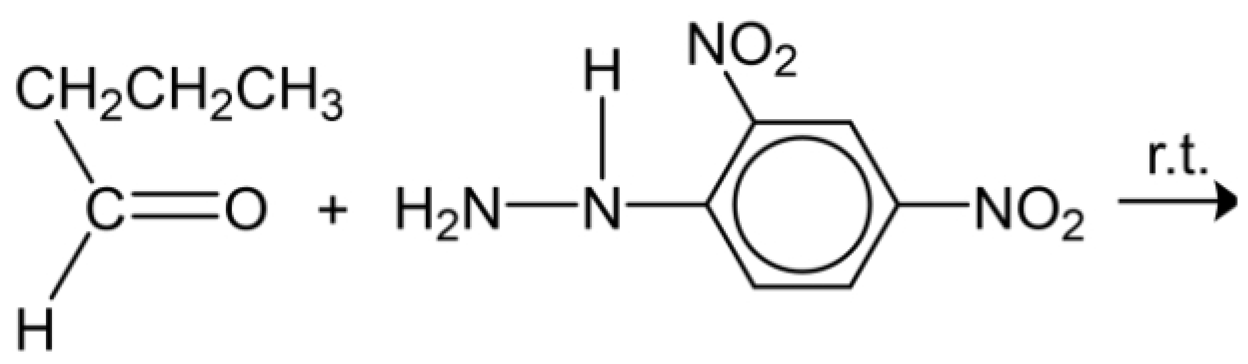
Note:

- A positive test with 2,4-DNPH gives an orange precipitate of dinitrophenylhydrazone.
- Other C=O containing functional groups (*e.g.* **carboxylic acid, ester, amide** and **acyl chloride**) will **not** give a positive test with 2,4-DNPH.

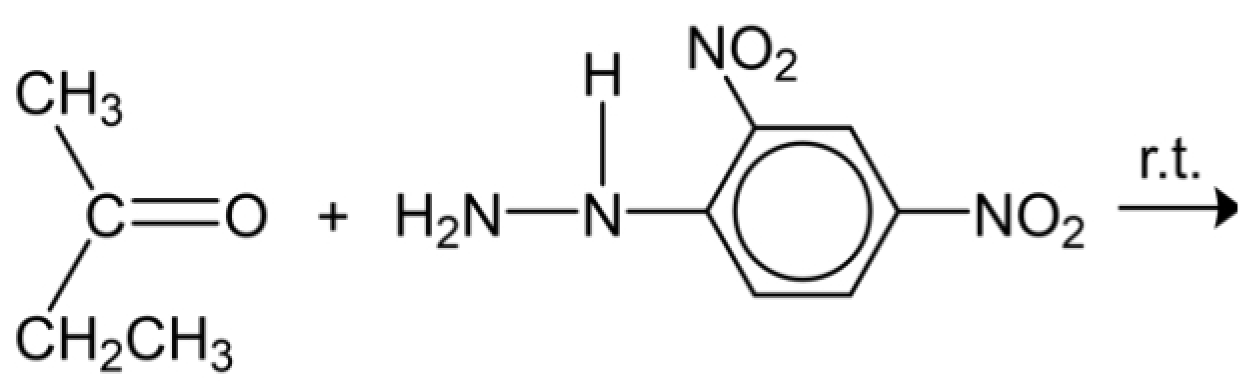
Self-Check 6A

Predict the products of the following reactions and write a balanced equation for each reaction.

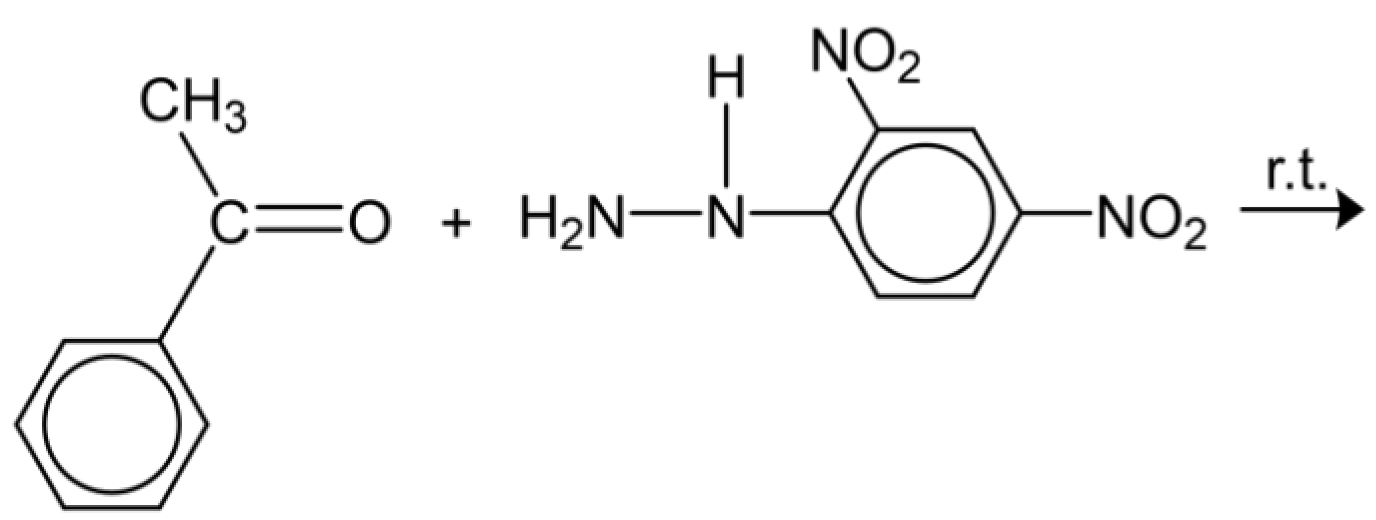
(a)



(b)



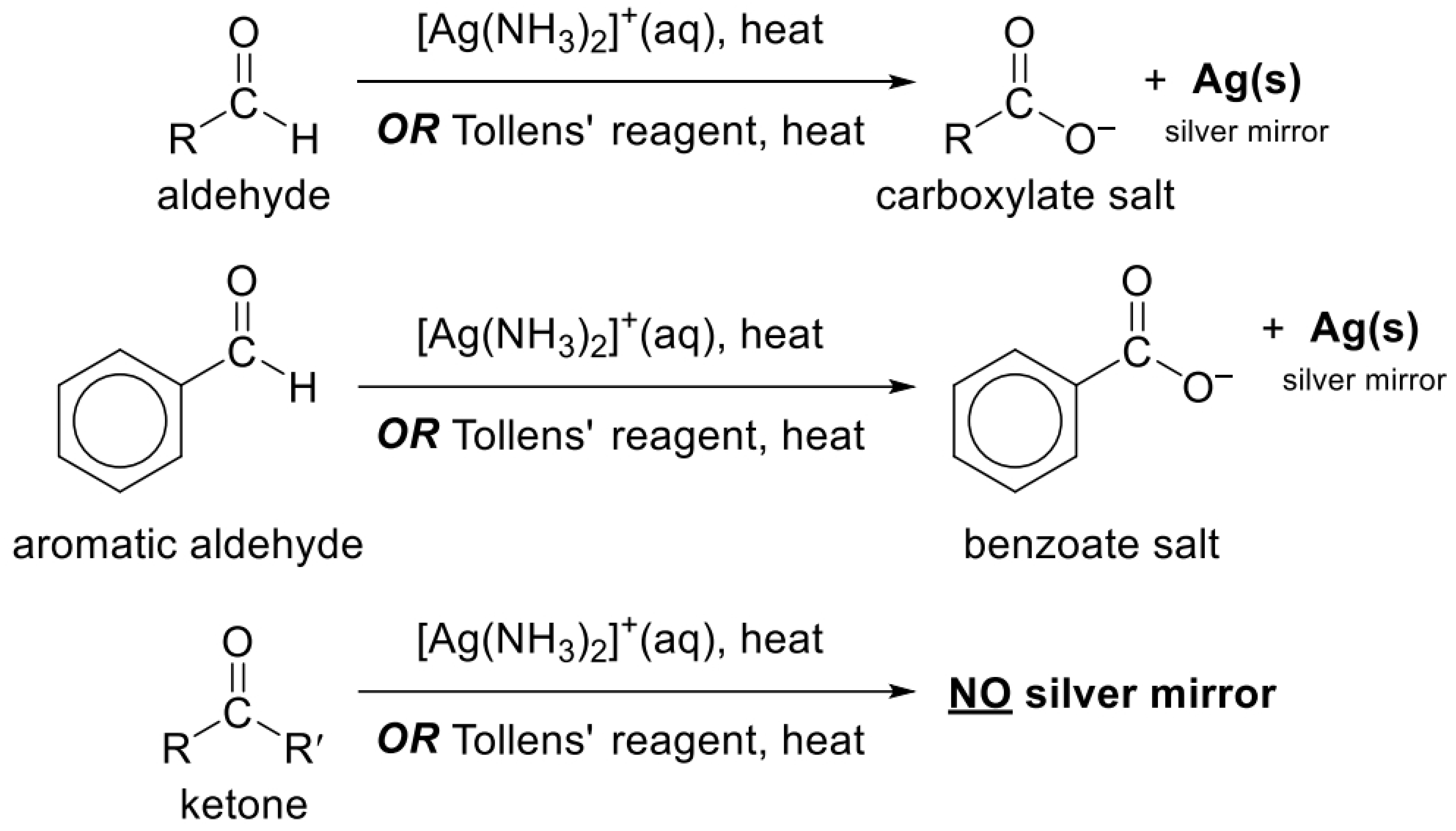
(c)



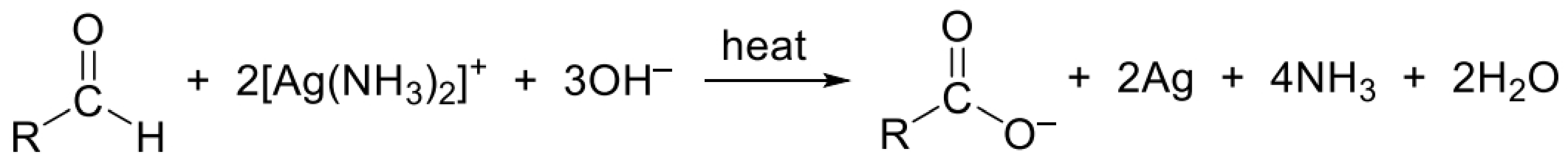
LO (e) deduce the nature (aldehyde or ketone) of an unknown carbonyl compound from the results of simple tests (*i.e.* Fehling's and Tollens' reagents; ease of oxidation)

6.2 Reaction with Tollens' Reagent (Silver Mirror Test)

❖ Identification Test for Aldehydes (Aliphatic & Aromatic)



Balanced equation:



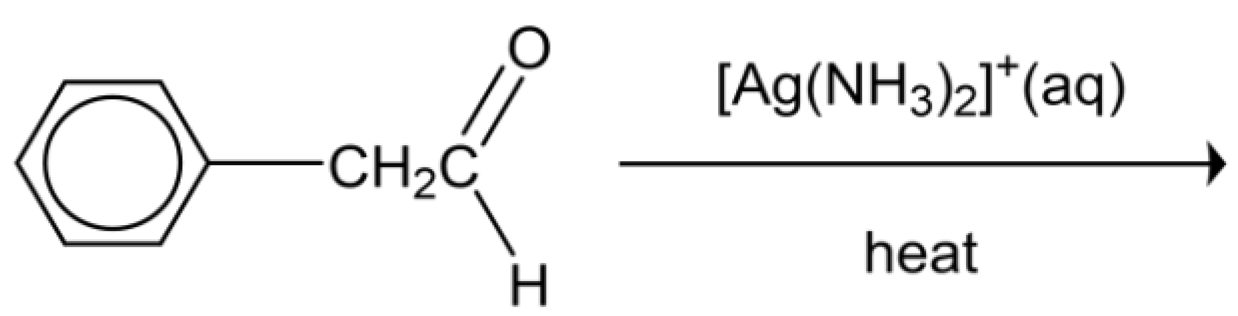
Reagents and conditions: Tollens' reagent (*or* $[Ag(NH_3)_2]^+$(aq), heat

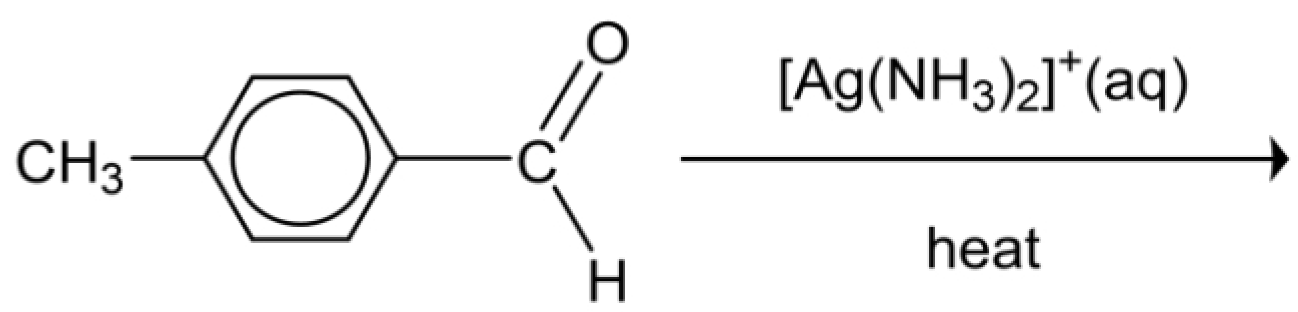
Observations: Silver mirror *or* grey/black ppt of Ag

Type of reaction: Oxidation

Example 6A

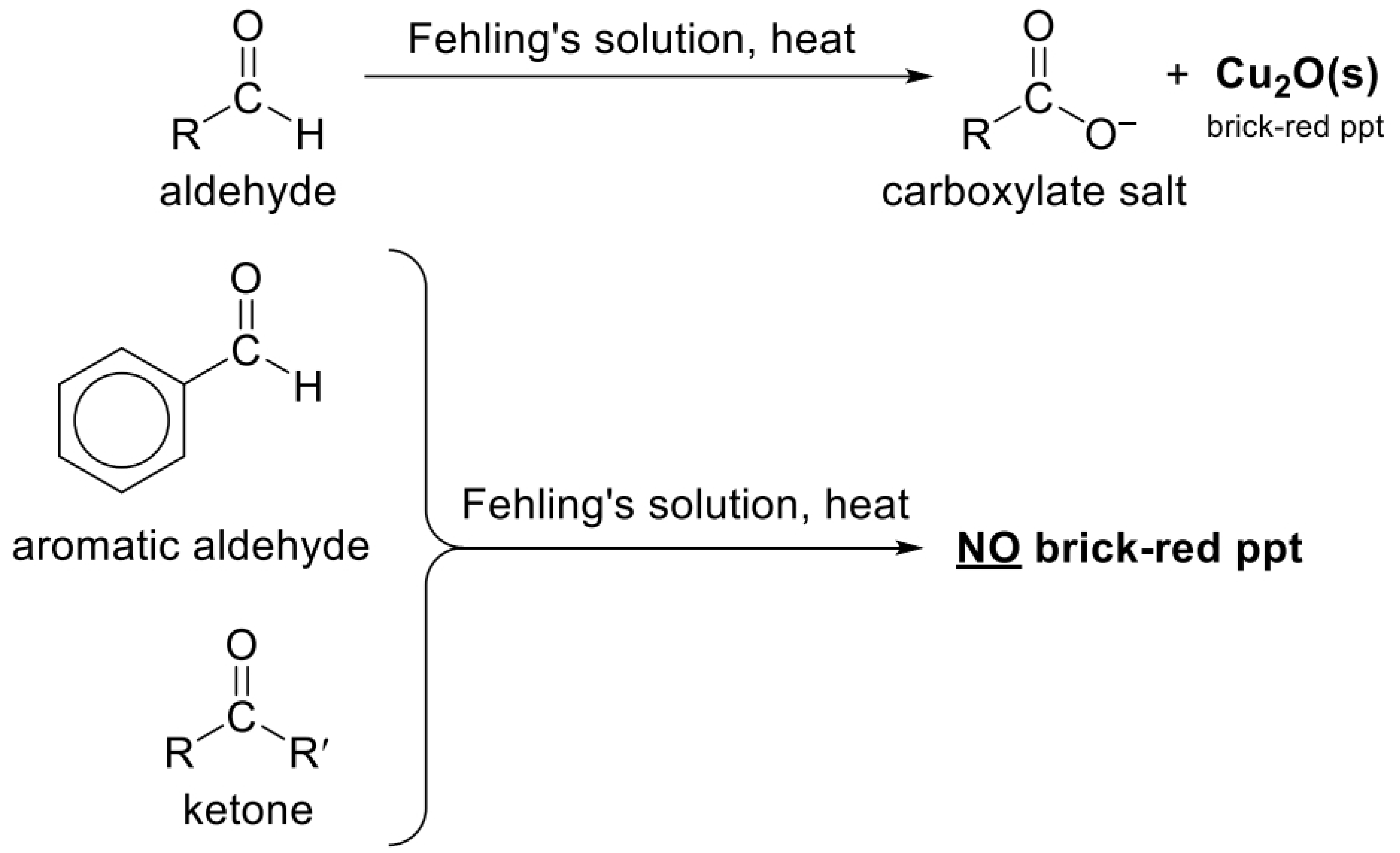
Draw the structural formula of the product(s) formed, if any.

(a) 

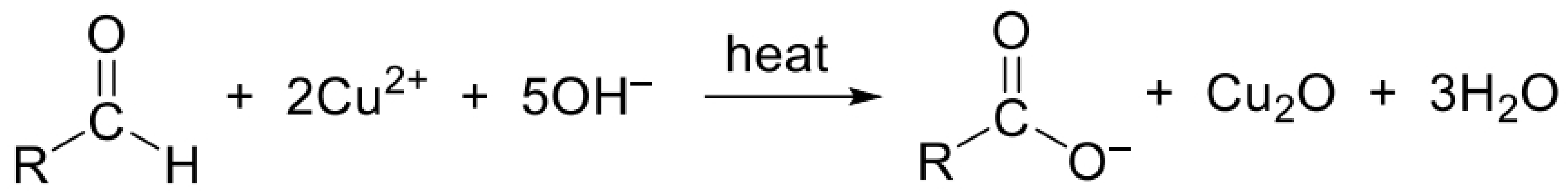
(b) 

6.3 Reaction with Fehling's Solution

❖ **Identification Test for Aliphatic Aldehydes**



Balanced equation:



Reagents and conditions: Fehling's solution, heat

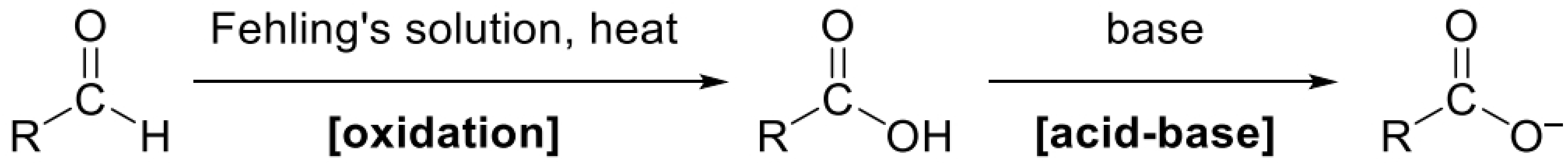
Observations: Brick-red ppt of Cu_2O

Type of reaction: Oxidation

Note:

1) Fehling's solution is an ***alkaline Cu^{2+} complex*** which is ***deep blue*** in colour.
2) This is a ***redox*** reaction since ***aldehyde is oxidised*** to carboxylic acid while the ***Cu^{2+} complex in the Fehling's solution is reduced*** to Cu_2O(s) (*i.e.* O.N. of Cu decreases from **+2 in deep blue Cu^{2+} complex to +1 in brick-red Cu_2O(s)**).

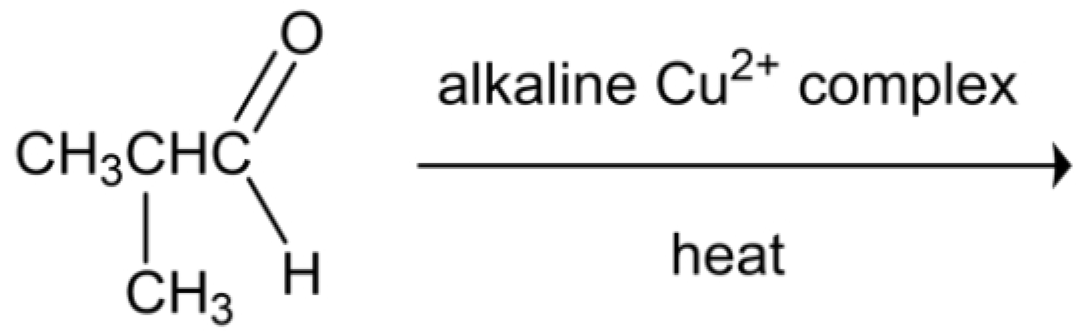
   The carboxylic acid formed then ***undergoes acid-base*** reaction with the base in the mixture.



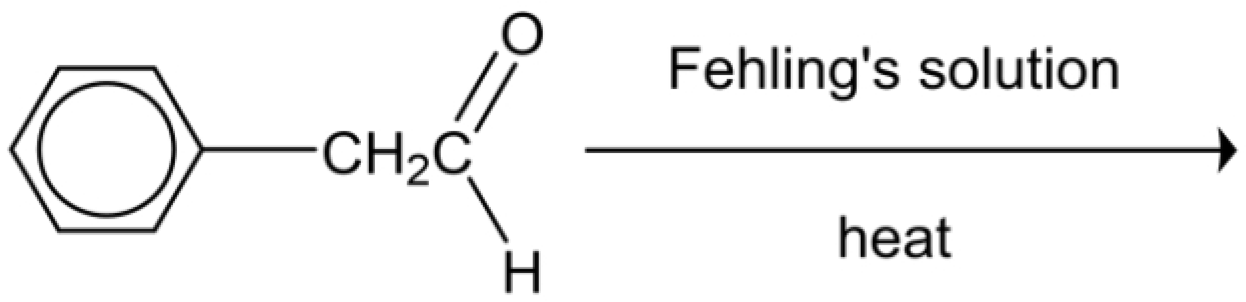
Example 6B

Draw the structural formula of the product(s) formed, if any.

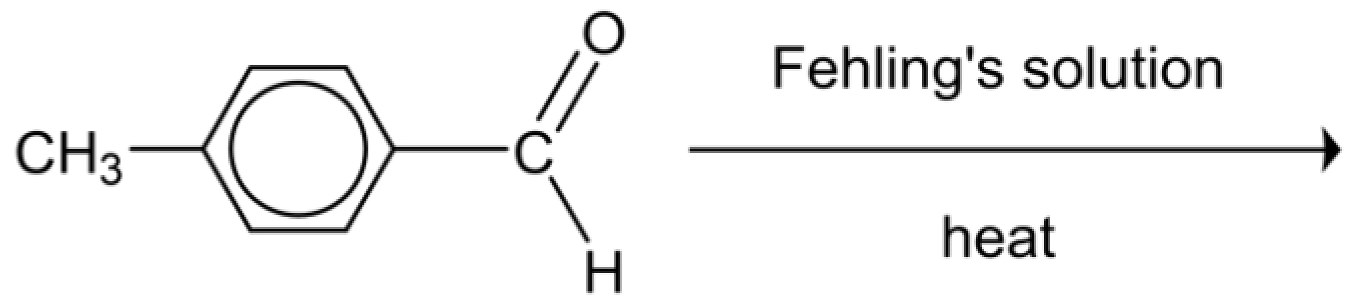
(a)



(b)



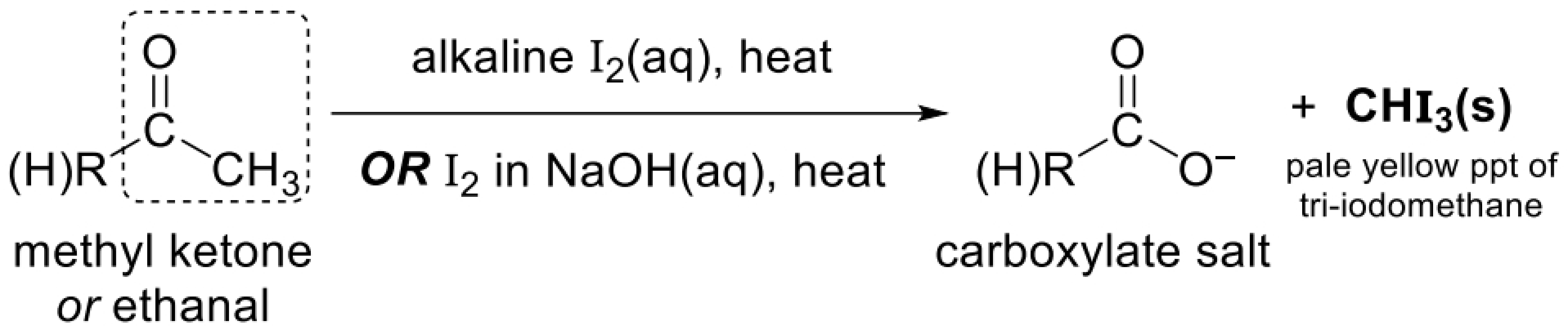
(c)



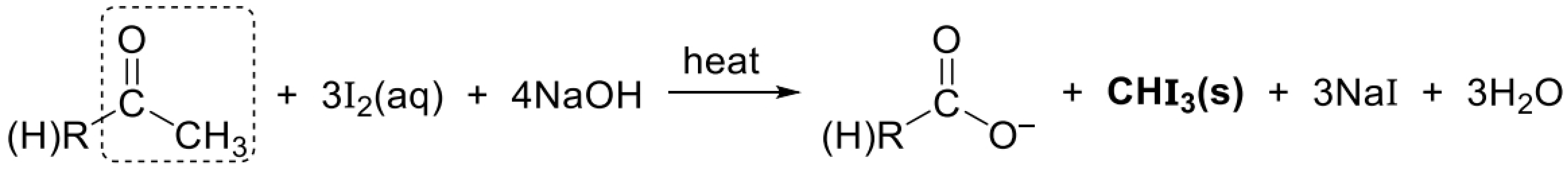
LO (f) deduce the presence of a CH_3CO— group in a carbonyl compound from its reaction with alkaline aqueous iodine to form tri-iodomethane

6.4 Tri-iodomethane (Iodoform) Test

❖ Identification Test for –$COCH_3$ group in Carbonyl Compounds



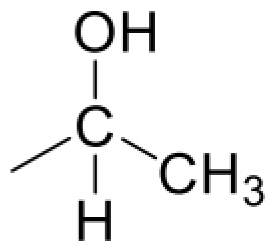
Balanced equation:

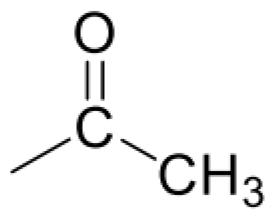


Reagents and conditions: I_2 in NaOH(aq), heat
Observations: Brown I_2(aq) is decolourised.
Pale yellow ppt. of tri-iodomethane, CHI_3
Type of reaction: Oxidation

Note:

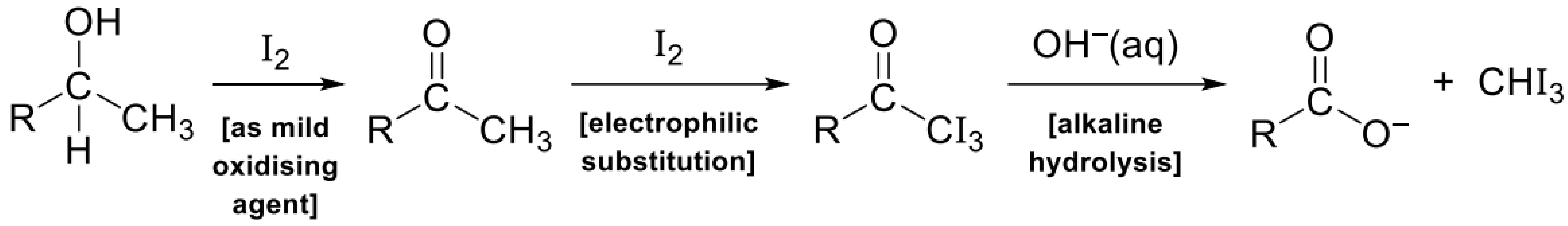
- This test specifically identifies the following structures:



in **alcohols** and


in **aldehydes** and **ketones**.

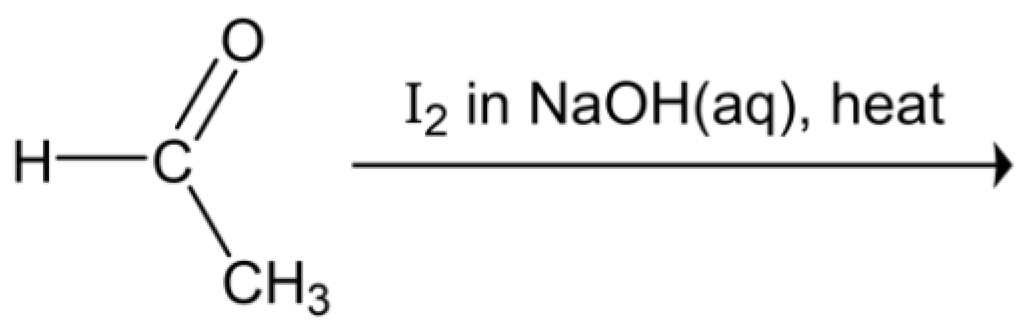
- I_2 acts as a mild oxidising agent, oxidising alcohols to aldehydes or ketones.

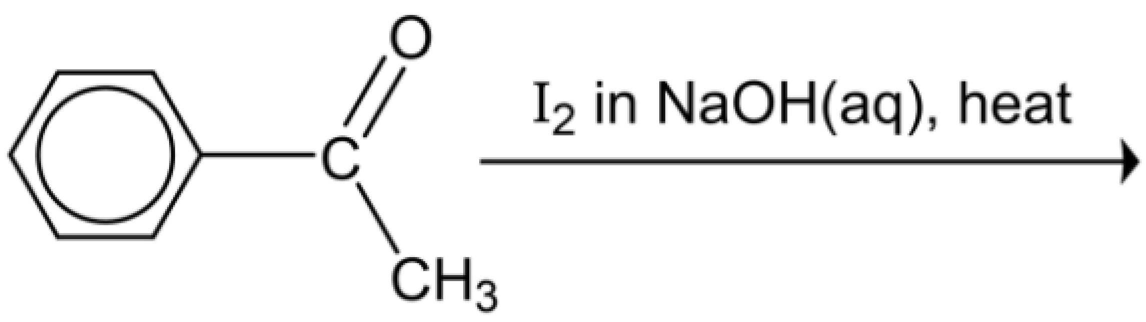


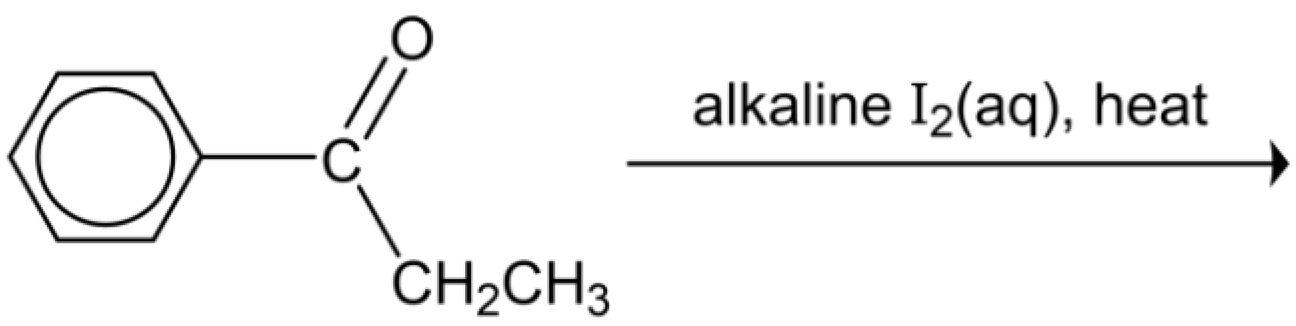
- The tri-iodomethane test involves breaking a C–C bond (*i.e.* shortens the carbon chain by one C atom and hence, it is a **step-down reaction**).
- Other $-COCH_3$ containing functional groups (e.g. **carboxylic acid, ester, amides** and **acyl chloride**) will **not** give a positive tri-iodomethane test.

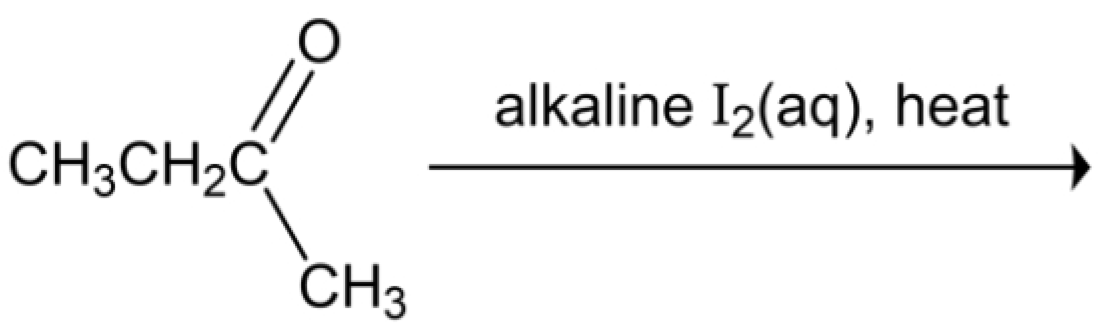
Self Check 6B

Draw the structural formula of the product(s) formed, if any.

(a)


(b)


(c)


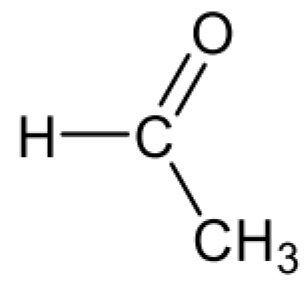
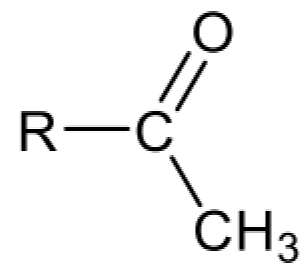
(d)


At the end of these sections, you should know that:

- The use of 2,4-DNPH, Tollens' reagent, Fehling's reagent and tri-iodomethane test can be used to differentiate carbonyl compounds from other functional groups.
- Tollens' and Fehling's reagents can be used to differentiate aldehydes from ketones.

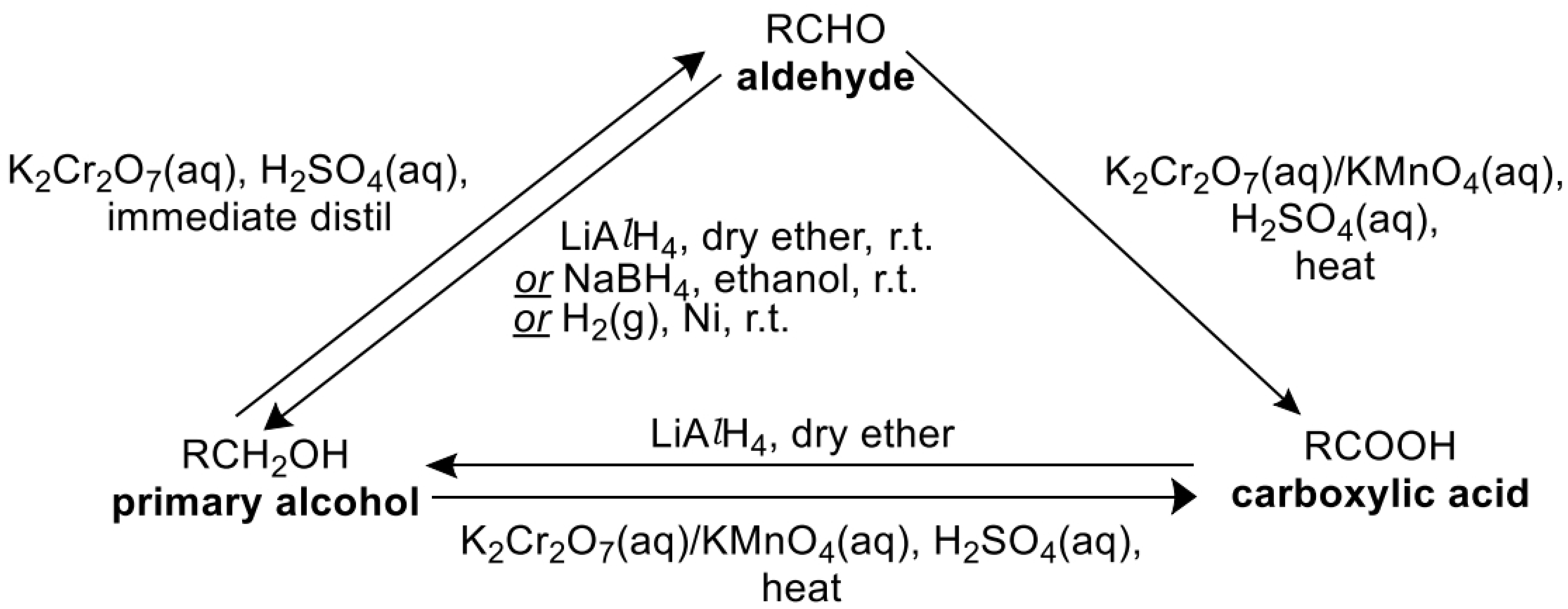
SUMMARY OF REACTIONS OF CARBONYL COMPOUNDS

SUMMARY OF IDENTIFICATION TESTS

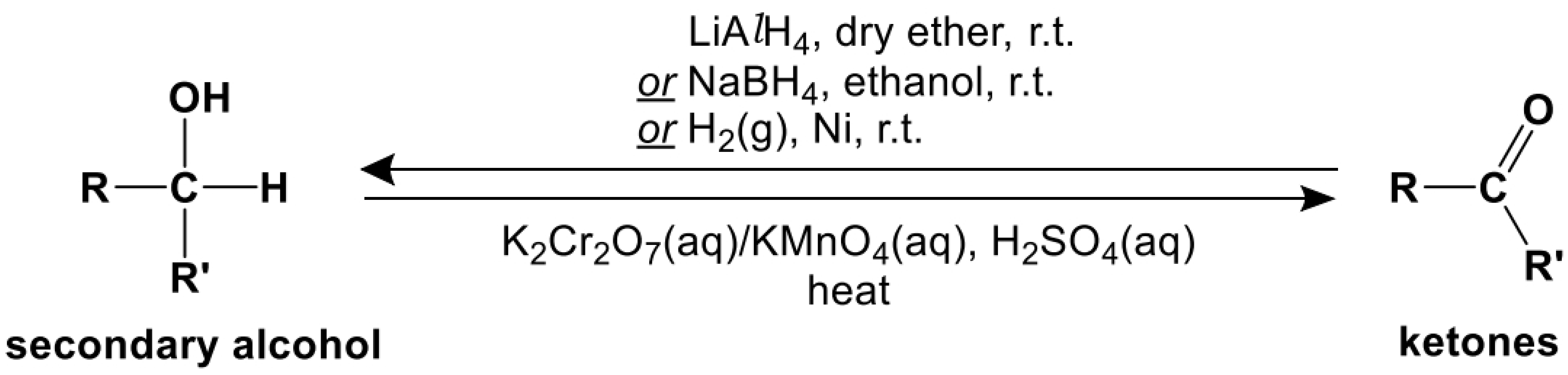
Reagent & Conditions	**2,4-DNPH**	**Tollens' reagent, heat**	**Fehling's solution, heat**	**I_2, NaOH(aq), heat**
Type of reaction	Condensation	Oxidation	Oxidation	Positive Iodoform test/ Oxidation
Observation	Orange ppt.	Silver mirror	Red-brown ppt.	Pale yellow ppt.
Aliphatic aldehydes	✓	✓	✓	✓ only for 
Aromatic aldehydes	✓	✓	✗	✗
Ketones	✓	✗	✗	✓ only for 

SUMMARY OF OXIDATION AND REDUCTION REACTIONS

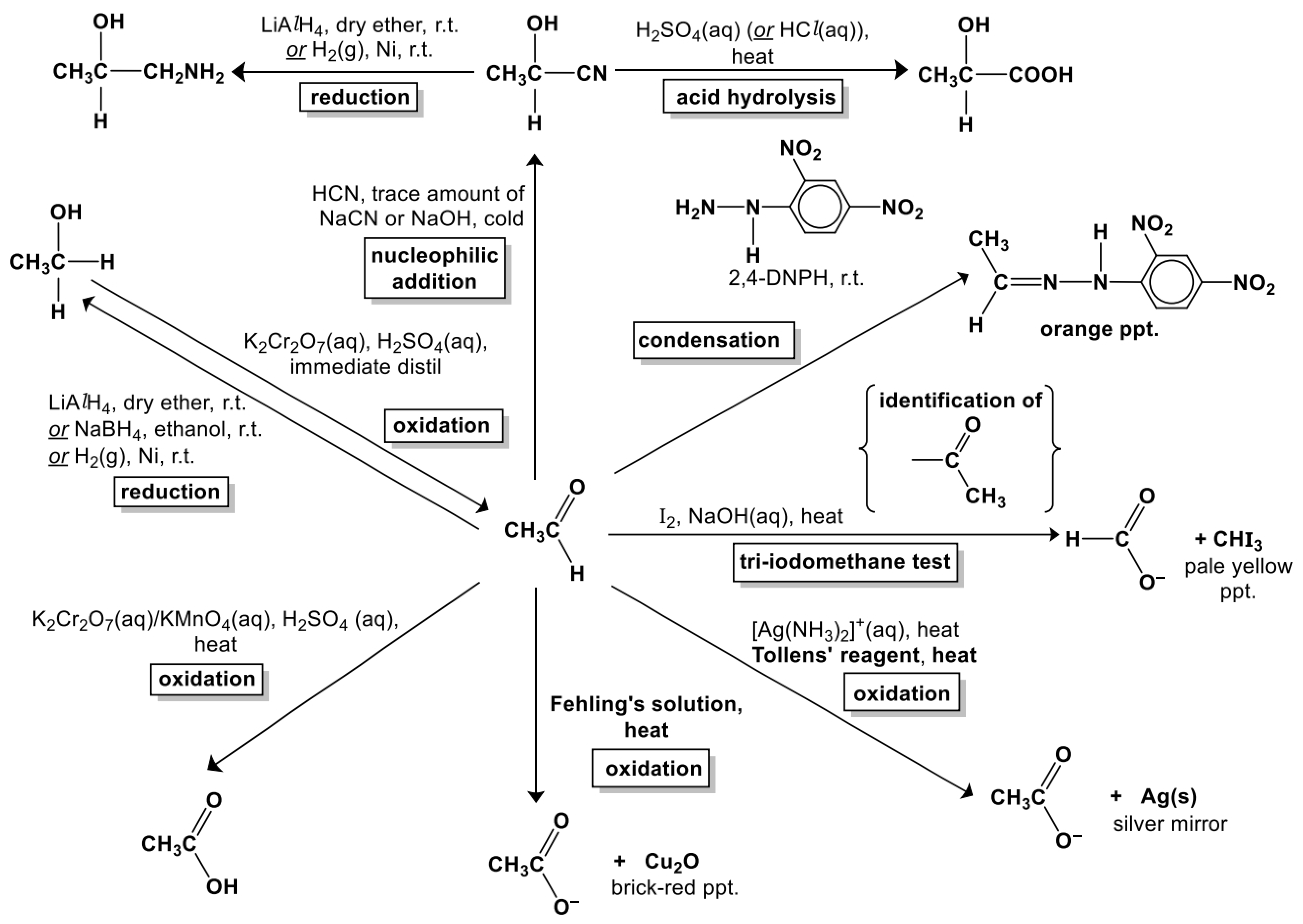
For aldehydes:



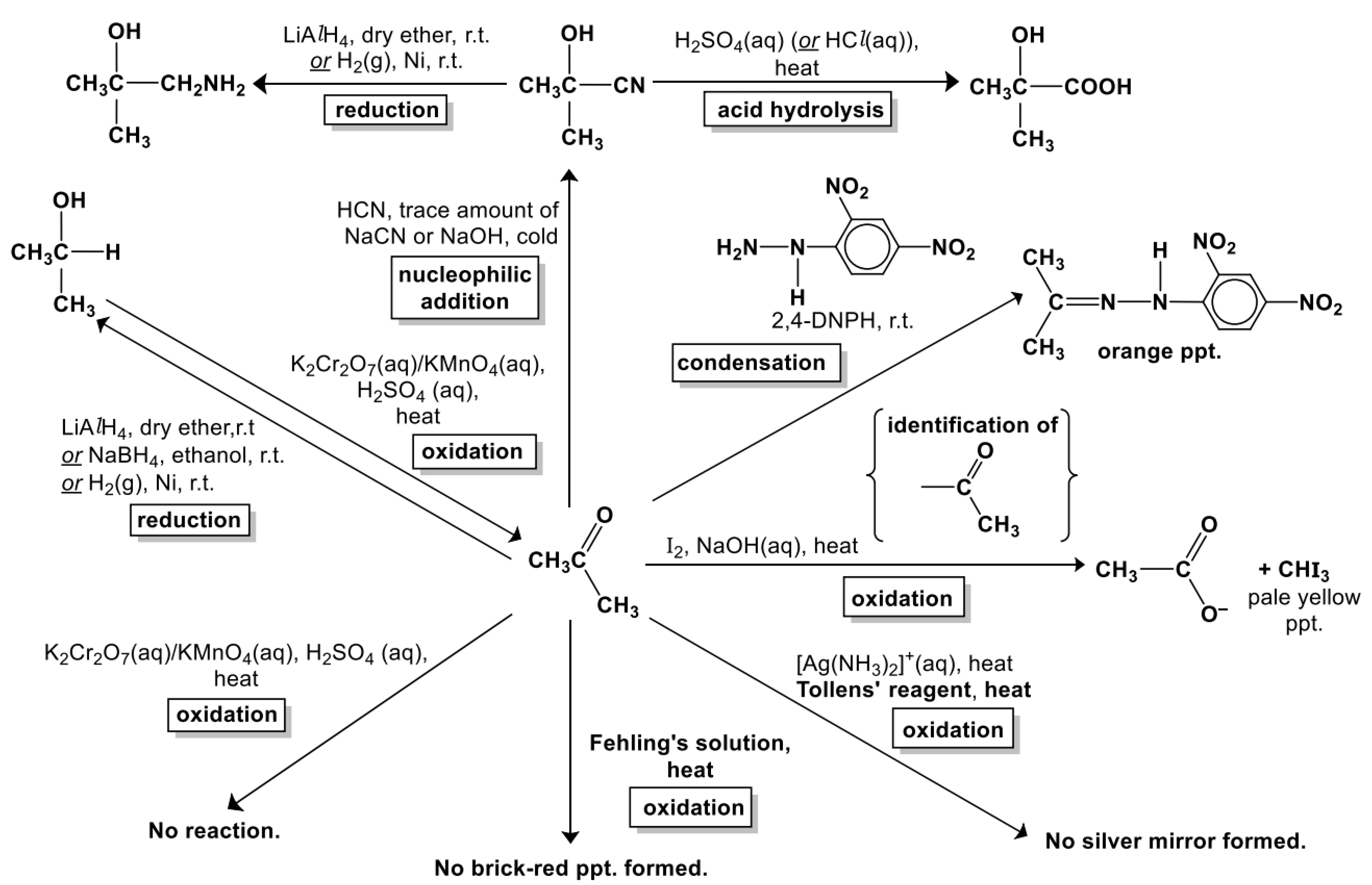
For ketones:



Reactions of Aldehydes (exemplified by ethanal, CH_3CHO):



Reactions of Ketones (exemplified by propanone, CH_3COCH_3):

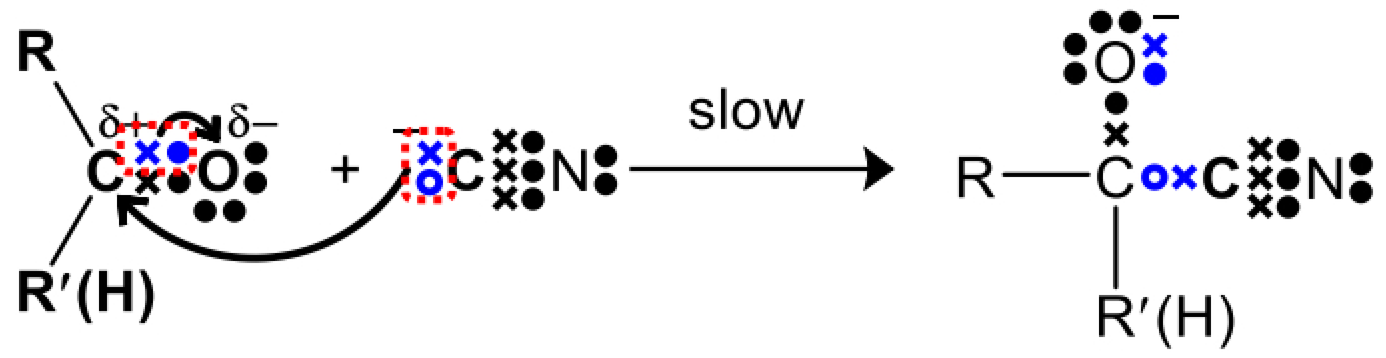


ANNEX A: ELECTRON MOVEMENT DURING NUCLEOPHILIC ADDITION MECHANISM & MECHANISM FOR THE REDUCTION OF CARBONYL COMPOUNDS

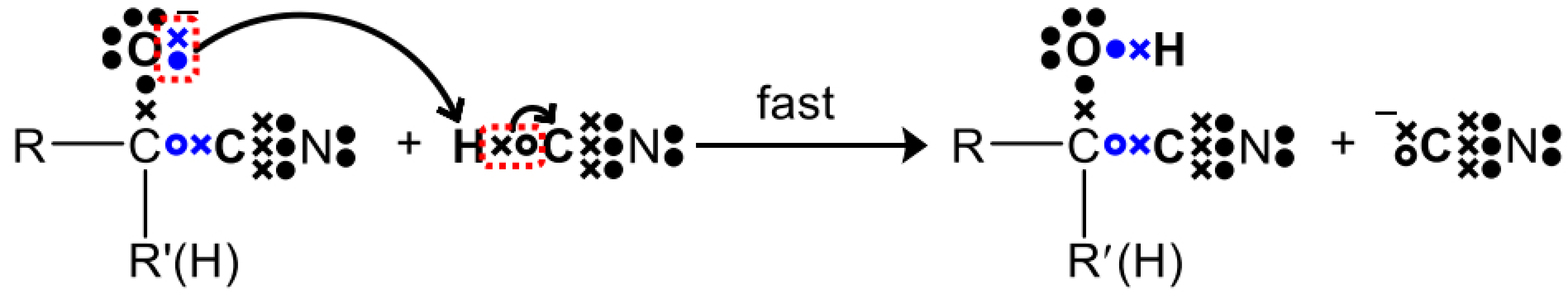
Movement of electrons during Nucleophilic Addition:

For your understanding only!! (do not include in mechanism answers)

Step 1:



Step 2:

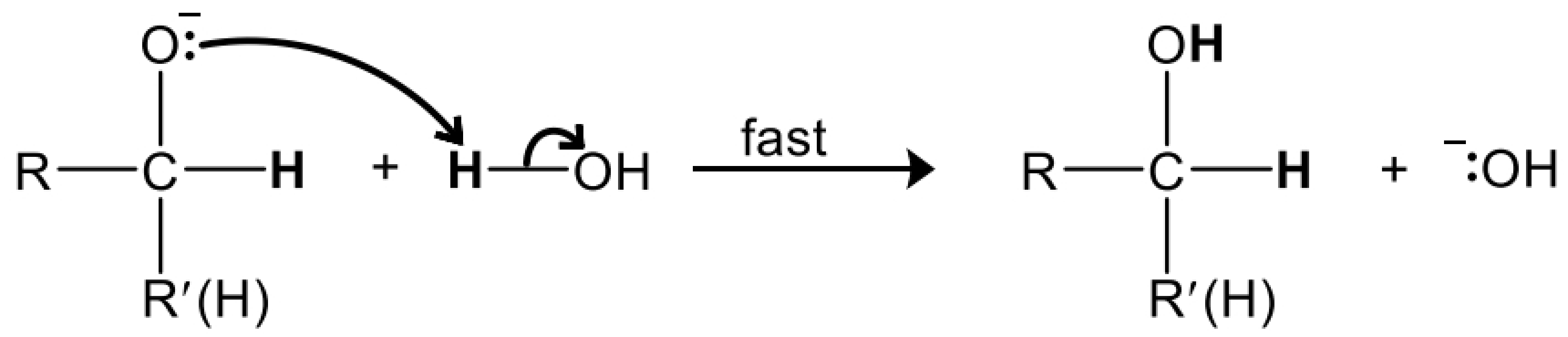


Mechanism of a Hydride Reduction of Carbonyl Compounds: *(NOT required in H2 syllabus)*

- Mechanism involved in Nucleophilic addition.
- Both $LiAlH_4$ and $NaBH_4$ provide **:H⁻** nucleophile to attack the electron-deficient $C^{\delta+}$ of C=O group.

The **:H⁻** nucleophile attacks electron-deficient $C^{\delta+}$ atom of C=O to form the alkoxide anion.

Step 2:



Water is then added to protonate the alkoxide anion to form alcohol.

ANNEX B: PREPARATION OF TOLLENS' REAGENT AND FEHLING'S SOLUTION

Tollens' reagent is unstable and must be freshly prepared.
A common preparation involves the following:

(a) Add a few drops of NaOH(aq) to $AgNO_3$(aq) to form brown silver(I) oxide ppt., Ag_2O(s).

$$2AgNO_3(aq) + 2NaOH(aq) \rightarrow Ag_2O(s) + 2NaNO_3(aq) + H_2O(l)$$

(b) Add NH_3(aq) dropwise until all ppt. is just dissolved to obtain a clear mixture containing $[Ag(NH_3)_2]^+$ complex ions.

$$Ag_2O(s) + 4NH_3(aq) + 2NaNO_3(aq) + H_2O(l) \rightarrow 2Ag(NH_3)_2NO_3 + 2NaOH(aq)$$

Fehling's solution is always freshly prepared in laboratory. It is made initially as two separate solutions, known as Fehling's A and Fehling's B.

Fehling's A: blue solution of $CuSO_4$
Fehling's B: colourless solution of potassium sodium tartrate (*i.e.* Rochelle salt) and strong alkali (e.g. NaOH(aq)).

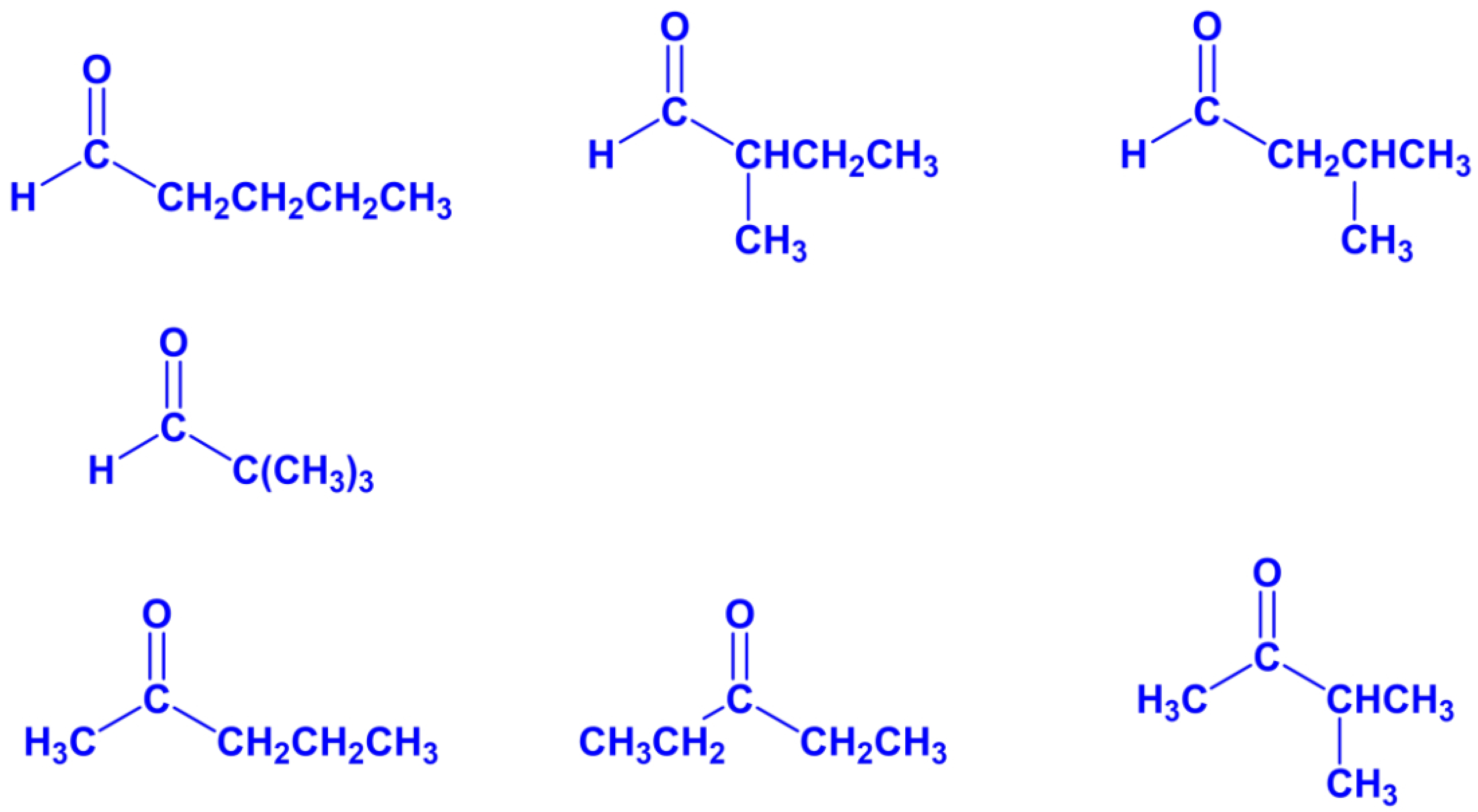
Equal volumes of two solutions are mixed to get the final deep blue Fehling's solution.

ANNEX C: ANSWERS TO SELF-CHECK QUESTIONS

Self Check 2A

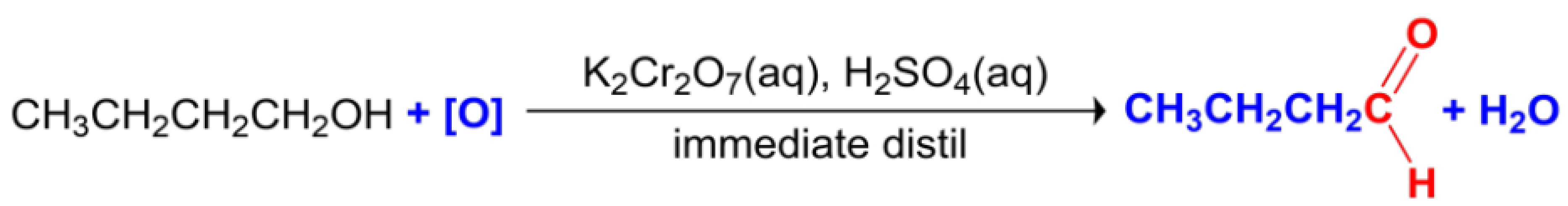
Draw all the structural isomers of $C_5H_{10}O$, each containing the carbonyl functional group.

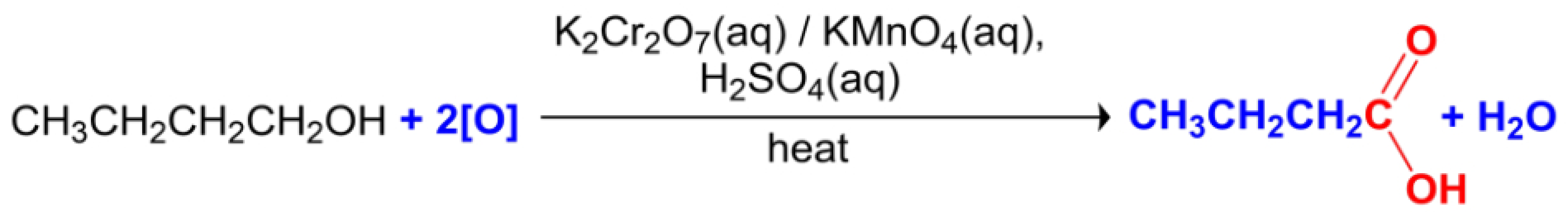
[*Hint: Aldehydes and ketones are isomeric (constitutional isomers) with one another.*]

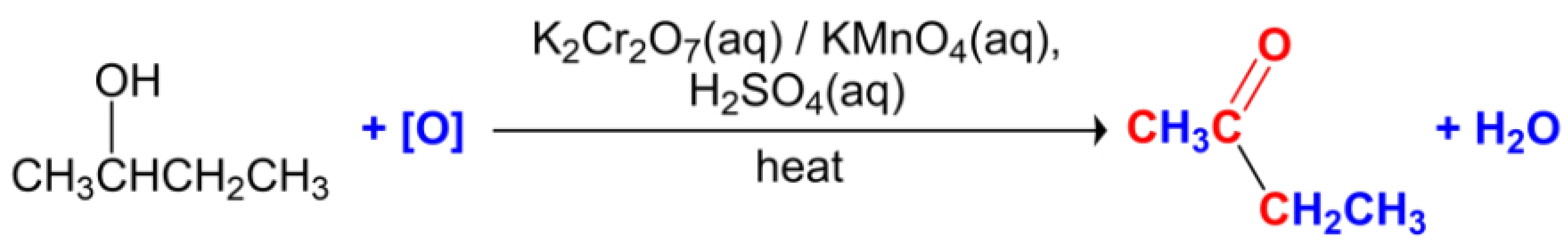


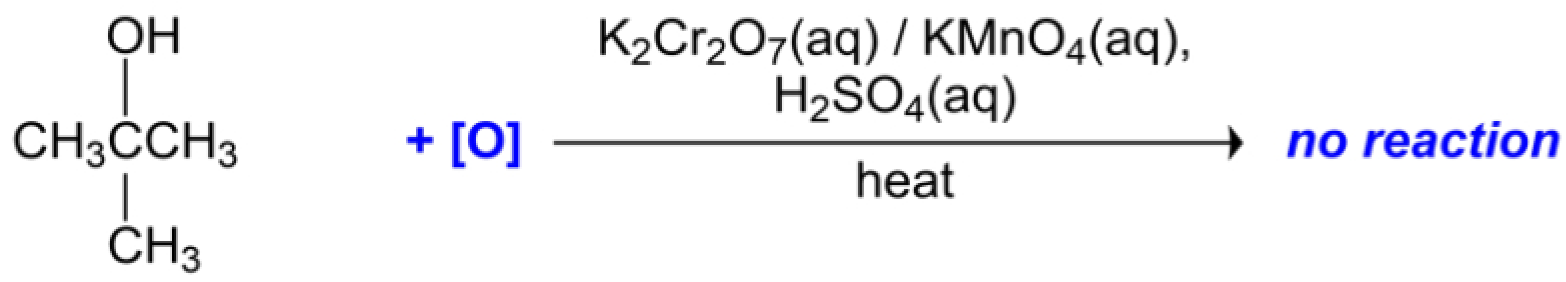
Self-Check 4A

Draw the structures of the products formed and balance the equation using [O].

(a)


(b)


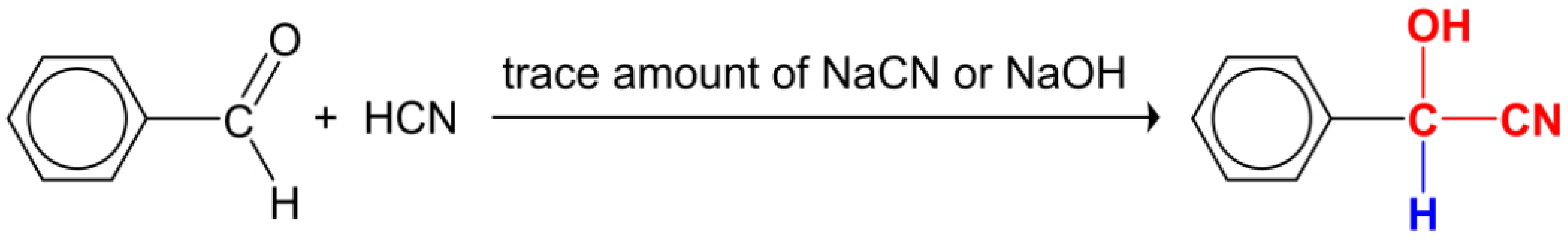
(c)


(d)


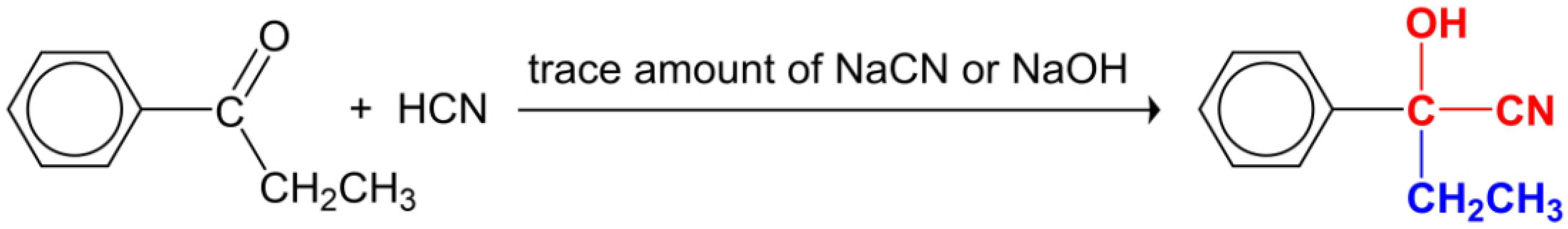
Self Check 5A

Predict the organic products of the following reactions.

(a)



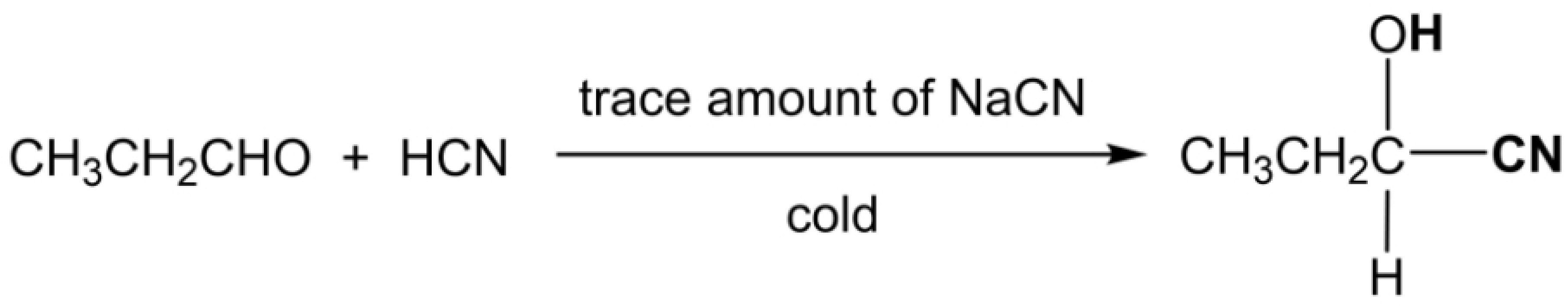
(b)



Self Check 5B

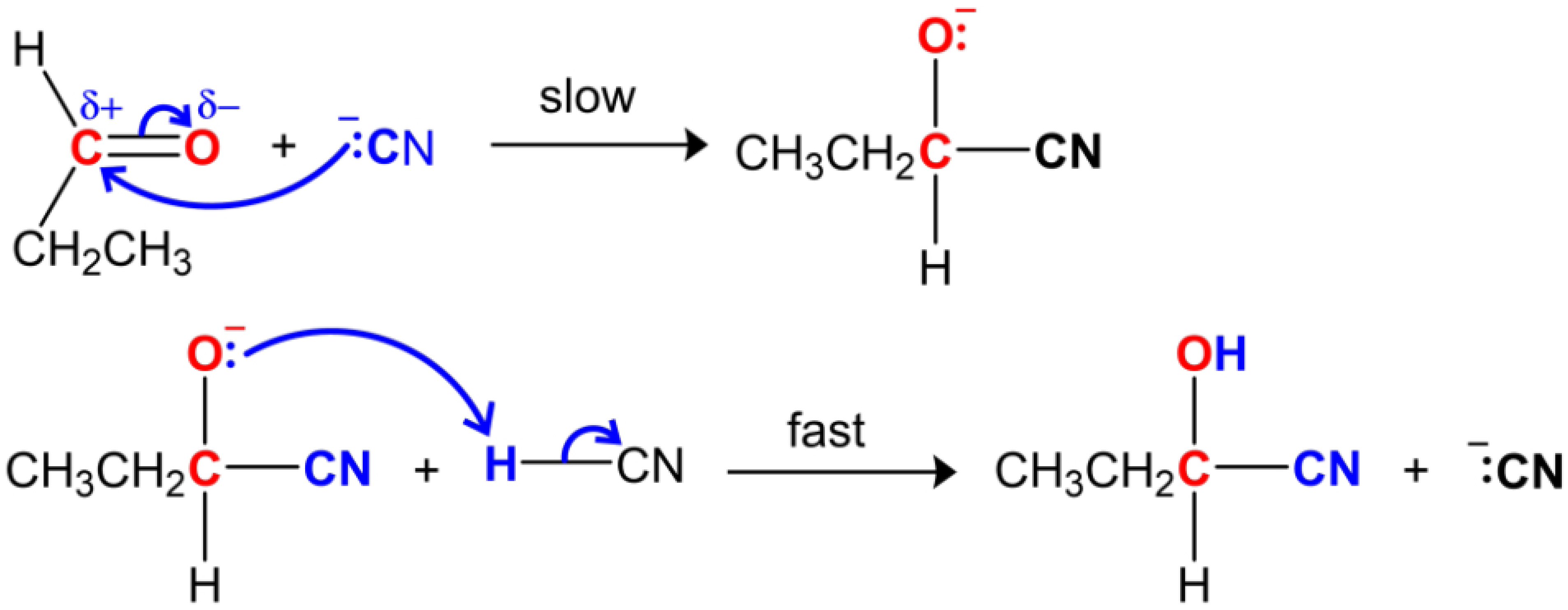
Predict the organic product and outline the mechanism of the reaction involved.

(a)

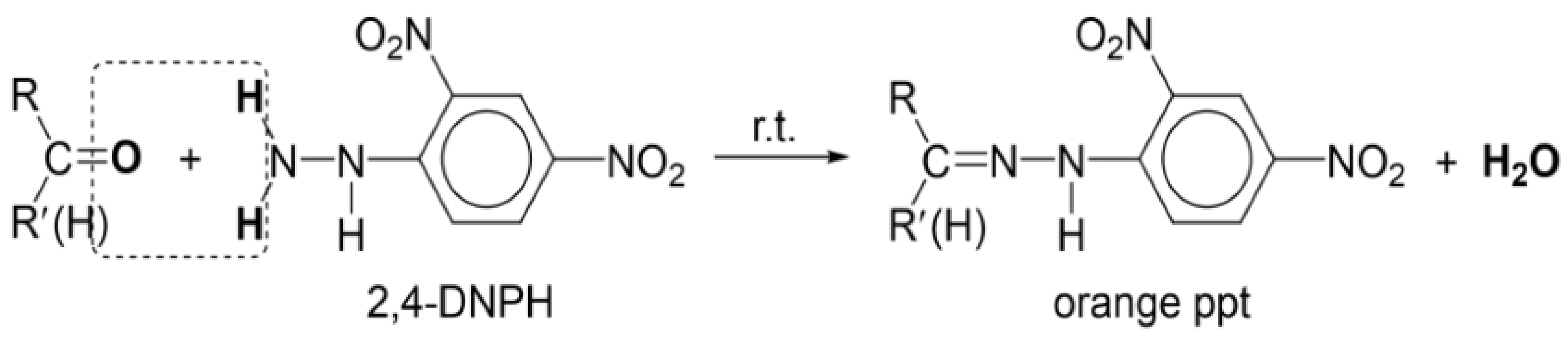


Mechanism : **Nucleophilic addition**

$$NaCN \longrightarrow Na^+ + CN^-$$

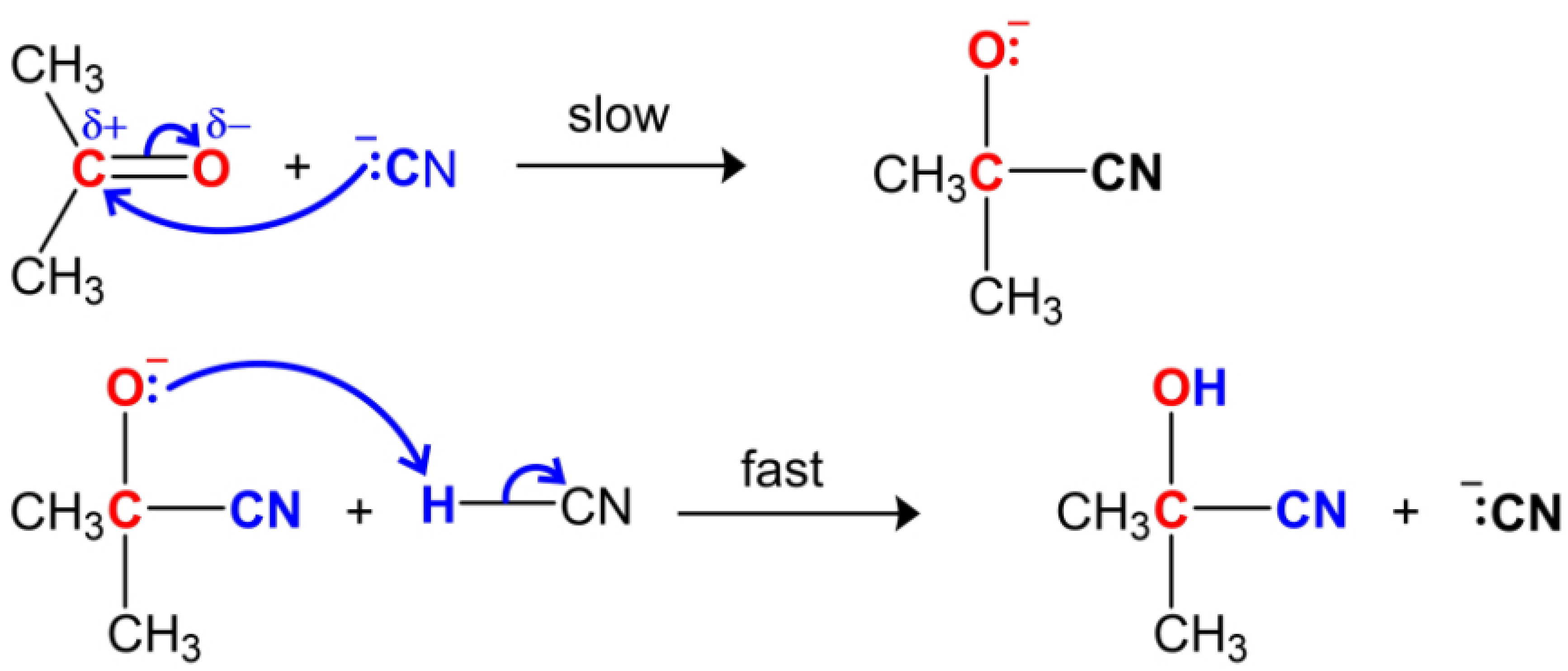


(b)



Mechanism : **Nucleophilic addition**

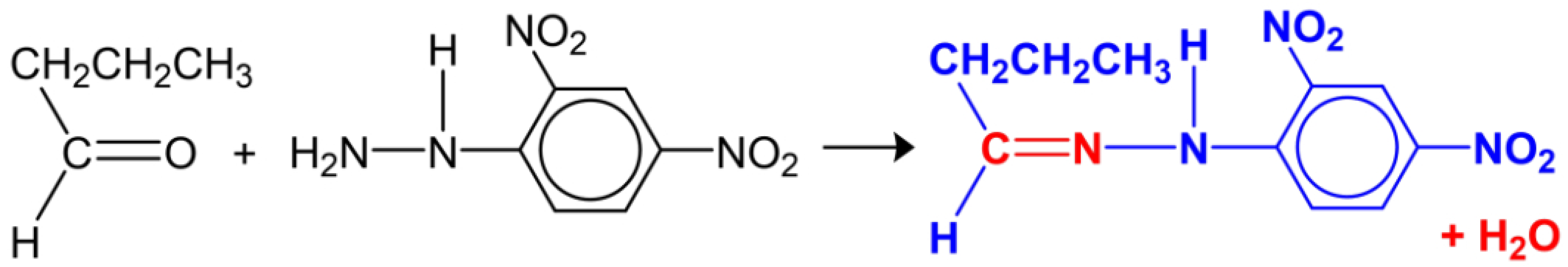
$$HCN + NaOH \longrightarrow Na^+ + CN^- + H_2O$$



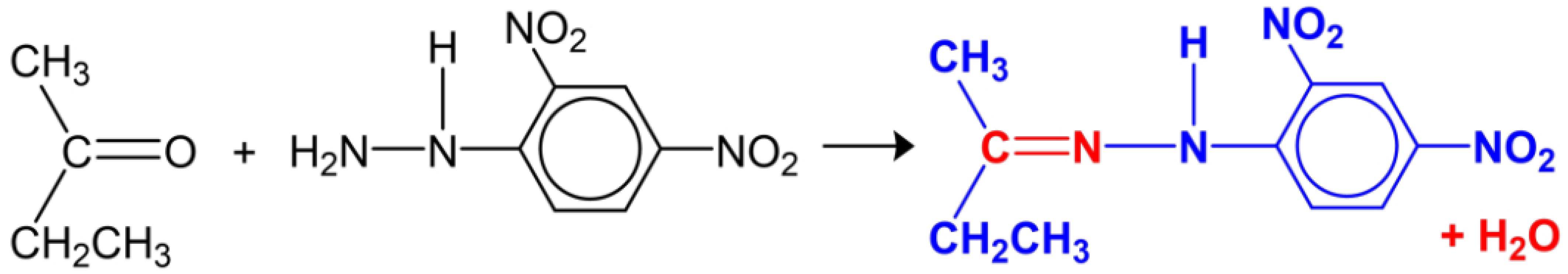
Self-Check 6A

Predict the products of the following reactions and write a balanced equation for each reaction.

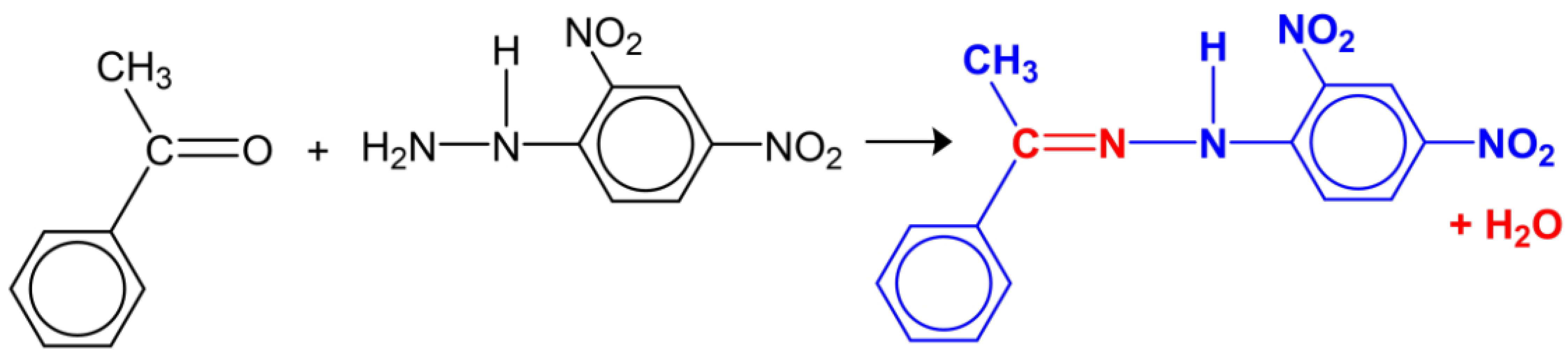
(a)



(b)



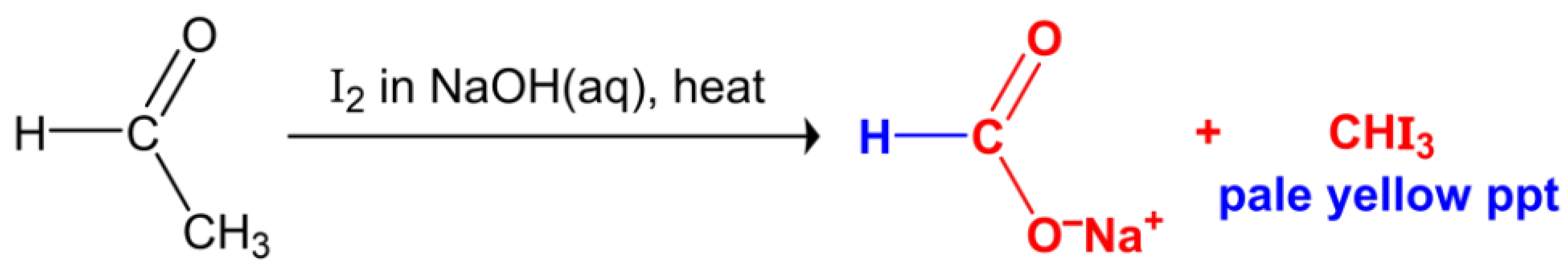
(c)



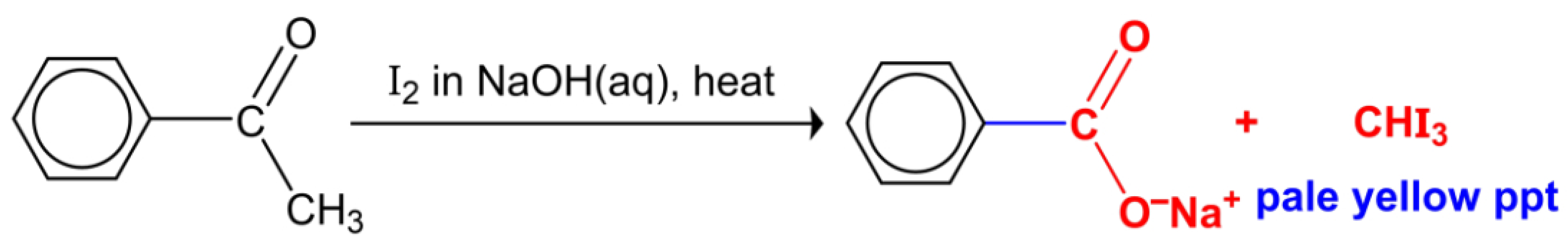
Self Check 6B

Draw the structural formula of the product(s) formed, if any.

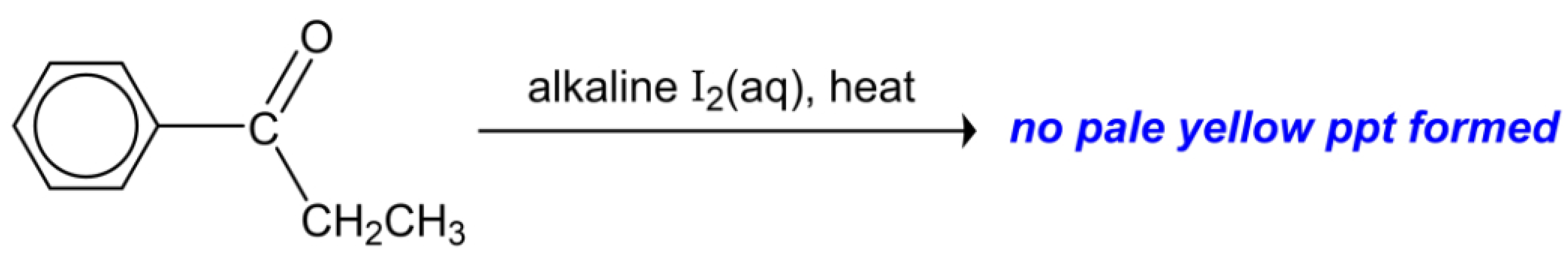
(a)



(b)



(c)



(d)