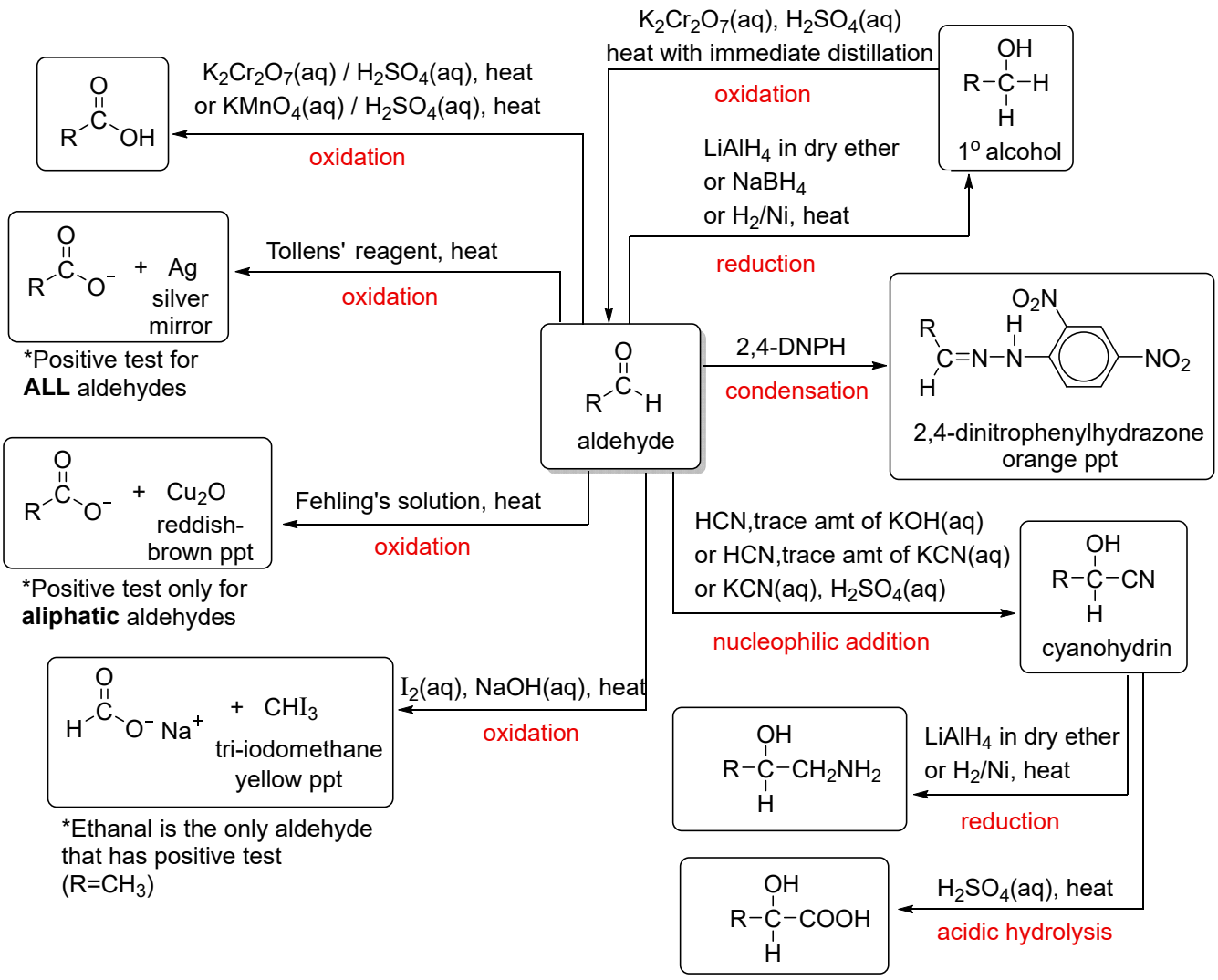
RAFFLES INSTITUTION
YEAR 6 H2 CHEMISTRY 2025
Tutorial 18 Carbonyl Compounds

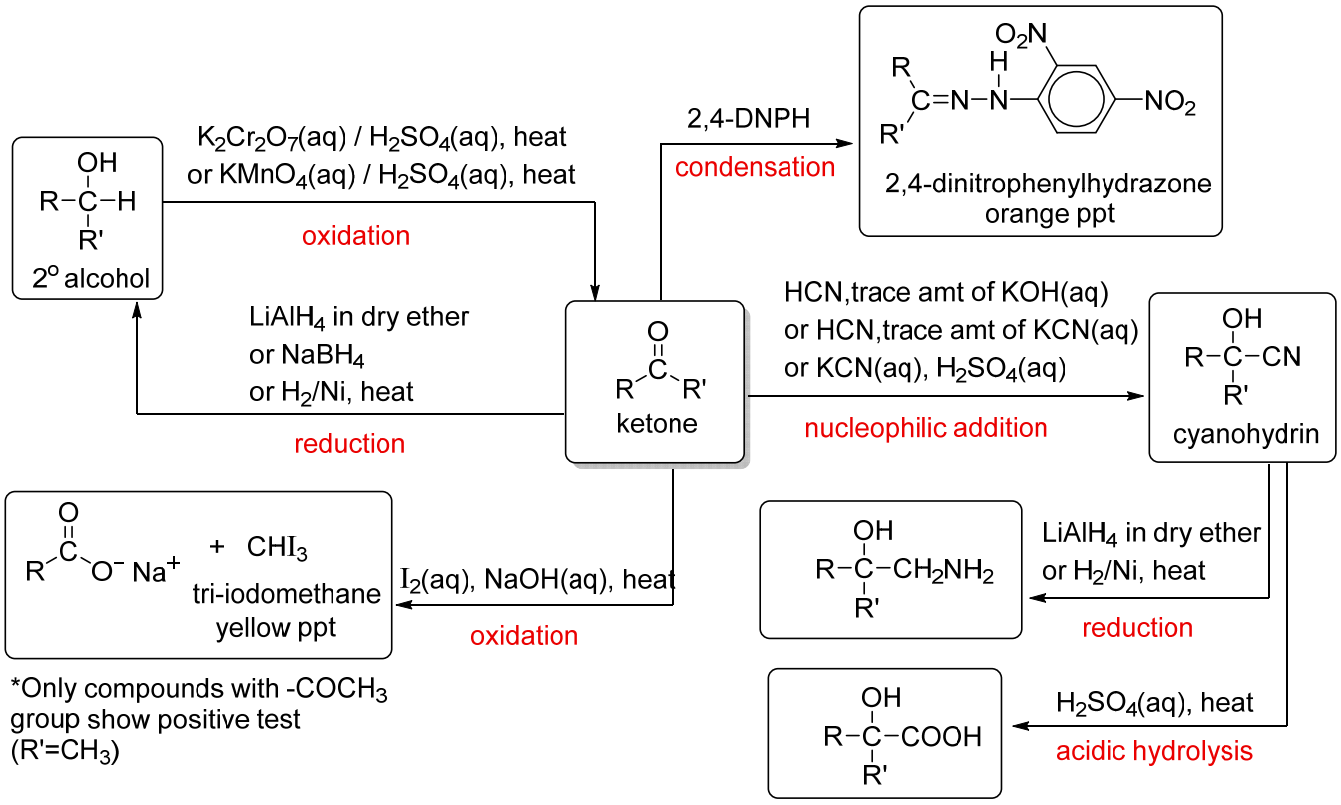
Reaction Mindmaps

❑ Aldehydes



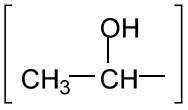
Note: Alcohols with $CH_3-CH(OH)-$ also give yellow ppt of CHI_3 when heated with I_2(aq) and NaOH(aq)

❑ Ketones



*Only compounds with -$COCH_3$ group show positive test ($R'=CH_3$)

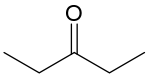
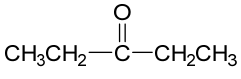
Notes:

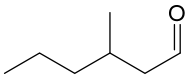
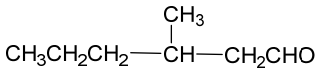
1) Alcohols with  also give yellow ppt of CHI_3 when heated with I_2(aq) and NaOH(aq)

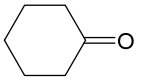
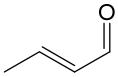
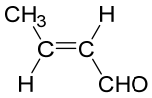
2) Aliphatic ketones generally do not undergo oxidation with Tollens' reagent, Fehling's solution, hot acidified $K_2Cr_2O_7$ and hot acidified $KMnO_4$.

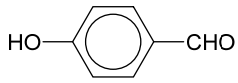
Answers to self-check questions

Q1

(a)  or 

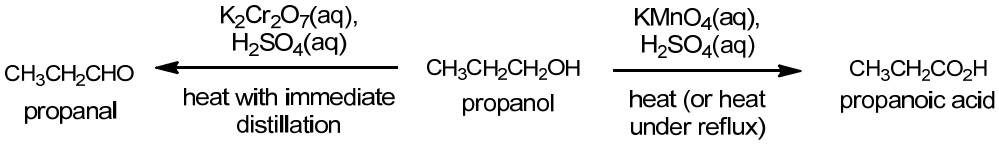
(b)  or 

(c)  (d)  or 

(e) 

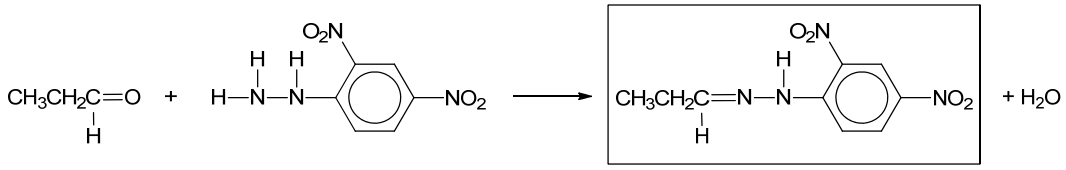
Q2(a) LiA*l*H_4 in dry ether, room temperature OR H_2(g), Ni(s), heat OR $NaBH_4$, room temperature

Q2(b)



Heat propan-1-ol with acidified $K_2Cr_2O_7$ carefully with immediate distillation of the product formed to collect mainly propanal as distillate.

Q2(c)



Observations: Orange ppt is formed.

Answers to MCQ: 3) B 4) C 5) B 6) D 7) B

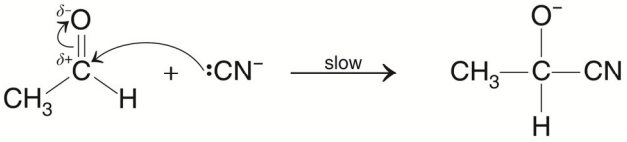
Suggested Solutions to Practice Questions:

1 (a) (i) Mechanism: Nucleophilic addition

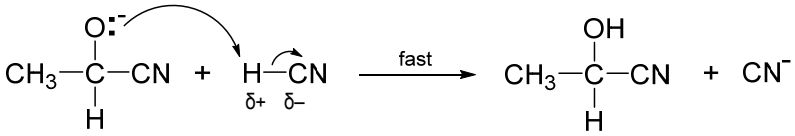
$NaCN(aq) \longrightarrow Na^+(aq) + CN^-(aq)$

> **NOTE**: HCN is a weak acid and hence a poor source of CN^- ion. The CN^- ion comes initially from the catalytic amount of NaCN(aq) added.
>
> **If *trace amt of NaOH* is used as catalyst:**
> $HCN + OH^- \rightarrow CN^- + H_2O$

Step 1



Step 2



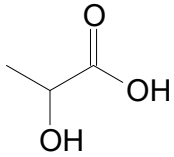
Checklist for nucleophilic addition mechanism:
- ☐ Name of mechanism
- ☐ δ+ on C, δ– on O in step 1 and δ+ on H, δ– on C in step 2
- ☐ Lone pair of electrons on Nu
- ☐ Curly arrows to show flow of electrons
  - Lone pair on Nu to δ+ C
  - C=O bond to δ– O
  - Lone pair on O^- to H (of HCN)
  - H–C bond to C
- ☐ Label slow/fast steps

(ii) NaCN provides the initial CN^- ions for the nucleophilic attack on the carbonyl carbon. HCN is used in the second step as a (Bronsted) acid to protonate the anionic intermediate.

Note: Do NOT merely say that NaCN helps to increase the rate of reaction and HCN is the reagent, as the question is about the roles of NaCN and HCN **in the mechanism**.

(iii) The carbonyl carbon in CH_3CHO is bonded to one alkyl group while that in $(CH_3)_2CO$ is bonded to two alkyl groups. Hence, the carbonyl carbon in $(CH_3)_2CO$ is less electron deficient (less $\delta+$) due to the additional electron donating alkyl group. There is also greater steric hindrance about the carbonyl carbon in $(CH_3)_2CO$ which hinder the approach of the attacking nucleophile. Therefore, propanone, $(CH_3)_2CO$, reacts at a slower rate than ethanal, CH_3CHO.

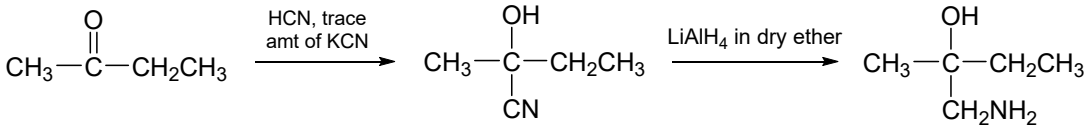
(b) Acidic hydrolysis reaction



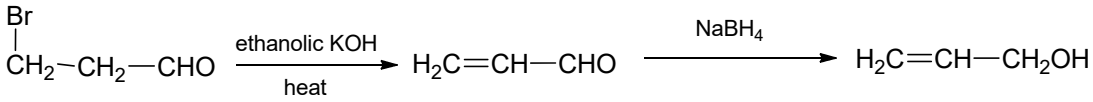
(c) (i) Lactic acid has a chiral carbon and no plane of symmetry through the molecule. Lactic acid in milk rotates the plane of polarised light because only 1 enantiomer is present (i.e. all the molecules present are of the same chirality).

(ii) In the slow step, the CN^- nucleophile can attack the planar carbonyl carbon of ethanal from either side with equal probability, resulting in the formation of a racemic mixture of two enantiomers, thus optical activity cancels out.

2 (a)

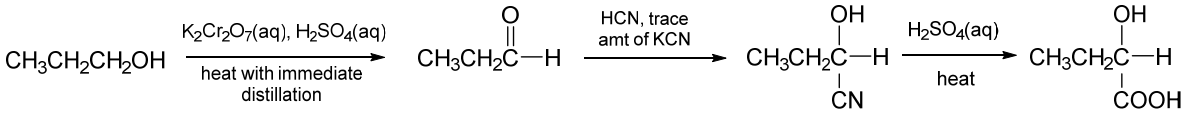


(b)

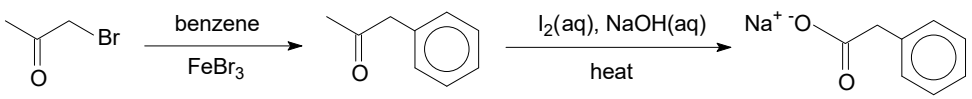


Note that the second step cannot be carried out using H_2 and Ni with heat, as the alkene group will also be reduced.
Alternatively, you may carry out reduction in the first step followed by elimination in the second step.

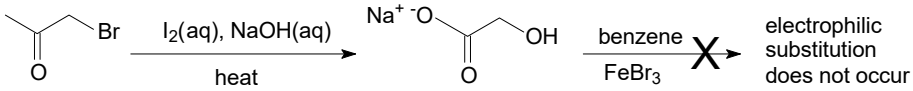
(c)



(d)

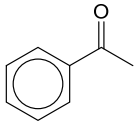
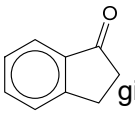


Note: The reagents and conditions for step 1 and step 2 cannot be interchanged as shown below.

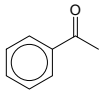


3 (a) Test
Add I_2(aq) and NaOH(aq) to each compound in a test-tube and heat in a hot water bath.

Observation


gives yellow ppt of CHI_3 while

gives no yellow ppt of CHI_3

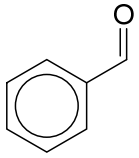
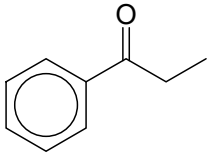
IMPORTANT NOTE:
Use of hot acidified $KMnO_4$ is not accepted because both compounds will undergo side-chain oxidation.


will give benzoic acid while

will give 1,2-benzenedicarboxylic acid.

(b) Test
Add Tollens' reagent to each compound in a test-tube and heat in a hot water bath.

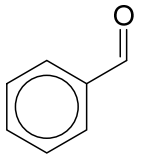
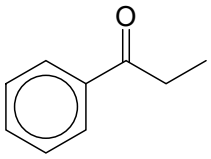
Observation


gives a silver mirror.

gives no silver mirror.

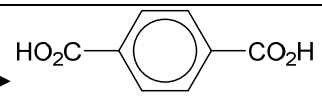
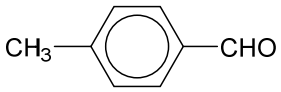
OR

Test
Add $K_2Cr_2O_7$ (aq), H_2SO_4 (aq), heat (DO NOT heat under reflux)

Observation

 will turn orange $K_2Cr_2O_7$ green while  will not produce a colour change.

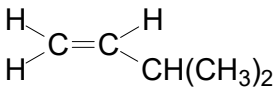
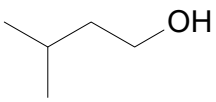
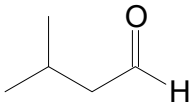
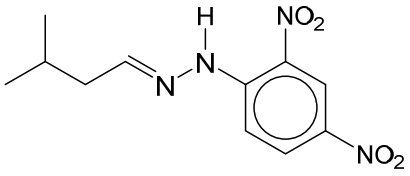
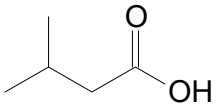
4 (a)

Evidence/Information	**Deductions**
A has molecular formula C_8H_8O	C to H ratio = 1:1 $\Rightarrow$ **A** likely contains a benzene ring
A $\xrightarrow{\text{2,4 DNPH}}$ orange ppt	Condensation (or addition-elimination) reaction **A** is an aldehyde or ketone.
A $\xrightarrow{\text{Tollens'}}$ Ag **A** $\xrightarrow{\text{Fehling's}}$ (no reaction)	**A** undergoes oxidation with Tollens' but not with Fehling's. **A** is an aromatic aldehyde.
A $\xrightarrow[\text{heat}]{\text{acidified } KMnO_4}$ 	Oxidation reaction. **A** has 2 substituents on the ring in the 1 and 4 position. $\Rightarrow$ **A** is 

(b)

Evidence/Information	**Deductions**
C $\xrightarrow{\text{2,4 DNPH}}$ orange ppt	Condensation (or addition-elimination) reaction. **C** is an aldehyde or ketone.
B (C_3H_8O) $\xrightarrow[\text{heat}]{\text{acidified } KMnO_4}$ C (C_3H_6O)	Oxidation reaction. **B** is a secondary alcohol and **C** is a ketone. (since there is no increase in number of oxygen atoms) $\Rightarrow$ **B** is  , **C** is  . **Note:** • If **B** was a primary alcohol, **C** would be a carboxylic acid with two oxygen atoms. • Also, **C** cannot be an aldehyde as any aldehyde group formed (from oxidation of a primary alcohol using $KMnO_4$) would be further oxidised to a carboxylic acid.

5 (a)

Evidence/Information	Deductions
A $\xrightarrow{\text{2,4 DNPH}}$ **B** (orange ppt)	Condensation (or addition-elimination) reaction **A** is an aldehyde or ketone.
A ($C_5H_{10}O$) $\xrightarrow[\text{heat}]{\text{acidified } K_2Cr_2O_7}$ **C** ($C_5H_{10}O_2$)	Compound **A** undergoes oxidation to give compound **C**. **A** is an aldehyde and **C** is a carboxylic acid. (Note: 1 oxygen atom in **A** to 2 oxygen atoms in **C**)
A $\xrightarrow{NaBH_4}$ **D**	Compound **A** undergoes reduction to give compound **D**, which is a primary alcohol.
D $\xrightarrow[\text{heat}]{Al_2O_3}$ **E**	Elimination of water from the primary alcohol to form a terminal alkene, **E**
E $\xrightarrow[\text{heat}]{\text{acidified } KMnO_4}$ $CH_3CH(CH_3)COOH$	Strong oxidation of the C=C in alkene **E**. Loss of one C atom as CO_2. Since CO_2 and 2-methylpropanoic acid are products of the oxidative cleavage of an alkene, **E** is   Hence, alcohol **D** is (a primary alcohol) **A** is  **B** is  **C** is 

(b) H is more electronegative than A*l* and B. As the **electronegativity difference between A*l* and H is greater than that between B and H**, the A*l*-H bond is **more polar** than B-H bond. This makes the H in A*l*–H **more electron rich (more δ^-) and more nucleophilic** than the H in B–H. This allows $LiAlH_4$ to be a stronger reducing agent.

OR

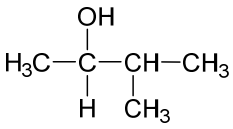
Since A*l* is larger than B, the **valence orbital used in bonding is more diffuse** for A*l* than B. The **orbital overlap is less effective** for the A*l*-H bond than the B-H bond, hence the A*l*-H bond is **weaker, losing the H^- nucleophile more readily**. Therefore, $LiAlH_4$ is the stronger reducing agent.

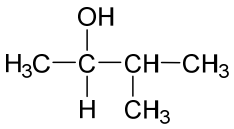
6 (a) Molecular mass of **K** is 86.

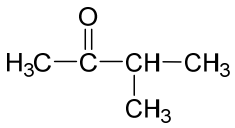
$86 - 16 = 70 = 12n + 2n \Rightarrow n = 5$

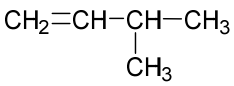
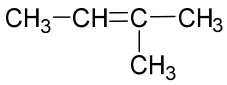
(b) Since **J** undergoes oxidation to give **K** with no change in number of O atom
$\Rightarrow$ **J** is a <u>secondary alcohol</u> and **K** a <u>ketone</u>.

Since **K** gives positive iodoform test $\Rightarrow$ **K** undergoes <u>oxidation</u> and contains <u>CH_3CO-</u> group.

J could be $CH_3CH(OH)CH_2CH_2CH_3$ or 

But **J** gives only 2 alkenes upon <u>elimination of H_2O</u>, thus **J** must be 

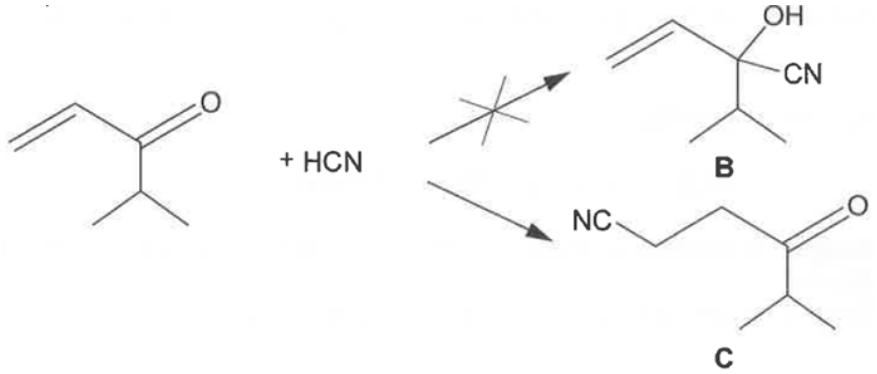
Therefore, **K** is 

The two alkenes from **J** are  

(no cis-trans isomerism in both compounds)

7 

1,3-butadiene does not undergo nucleophilic addition reaction with HCN <u>due to the absence of an electron deficient C</u> (δ+ C) to attract the CN^- nucleophile.
(Note: Both C=C and C=O π bonds are electron rich. Hence it is <u>insufficient</u> to state that the C=C π electron cloud repel the nucleophile CN^- as carbonyl with C=O group can undergo nucleophilic addition reaction).



In 4-methyl-1-penten-3-one, the nucleophilic attack on the δ+ carbonyl C is <u>sterically hindered by the $-CH(CH_3)_2$ group</u>.

Also, the <u>p orbitals of the sp^2 C in C=C and C=O overlap</u> to form a <u>delocalised π electron cloud</u>. Due to the <u>highly electronegative O atom</u>, the delocalised π electron cloud is pulled towards the O atom and the <u>terminal alkene C becomes δ+</u>.

Hence, the nucleophile will attack the δ+ terminal alkene C instead, resulting in the nucleophilic addition occurring at the alkene group to form **C** instead of at the carbonyl group to form **B**.

Resonance structure and mechanism (**not required** in answer, only for further understanding)