: Oxidation :

- addition of oxygen/halogen.
- Loss of hydrogen.
- Loss of $\bar{e}$.

⇒ Alcohol
⇒ Aldehyde & ketone
⇒ Hydrocarbon
a) alkane
b) alkene
c) alkyne

: Alcohol Oxidation :

i) $RCH_2OH \xrightarrow{M.O.R} RCH=O$
1° Alcohol → aldehyde.

ii) $R_2CHOH \xrightarrow{M.O.R} R_2C=O$
2° Alcohol → ketone.

iii) $R_3C-OH \xrightarrow{M.O.R}$ can't be oxidised.
no α-H is present.

$RCH_2OH \xrightarrow{S.O.R} R-\overset{O}{\overset{\|}{C}}-OH$
1° Alcohol.

$R_2CHOH \xrightarrow{S.O.R} R_2C=O$.

$R_3C-OH \xrightarrow{S.O.R}$ can't be oxidised

Strong Oxidising reagents (examples):

i) $\overset{+7}{KMnO_4}$, H^+ (Purple/Pink)

ii) $K_2\overset{+6}{Cr_2}O_7$, H^+ (orange)

iii) $H_2\overset{+6}{Cr}O_4$. (yellow).

iv) CrO_3 + conc. H_2SO_4 (Jones reagent)

$RCH_2OH \xrightarrow[KMnO_4]{S.O.R} RCO_2H + Mn^{2+}$ (colorless)

Purple → colorless.

$R_2CHOH \xrightarrow{S.O.R} R-\underset{O}{\overset{}{C}}-R + Mn^{2+}$

Purple → colorless.

$R_3C-OH \xrightarrow{KMnO_4}$ no reaction at room temp.

$RCH_2OH \xrightarrow[+KOH]{KMnO_4} RCO_2\cancel{H}$ + $MnO_2\downarrow$ reddish brown ppt.

KMnO4

Purple ↓ colorless.

i) 1° Alcohol vs 3° Alcohol.
+ve test −ve test

ii) 2° Alcohol vs 3° Alcohol.
+ve test. −ve test.

$H_2CrO_4 \rightarrow Cr^{3+}$

(yellow) (green)

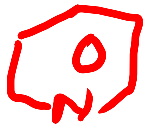
$K_2Cr_2O_7 \longrightarrow Cr^{3+}$ orange → green.

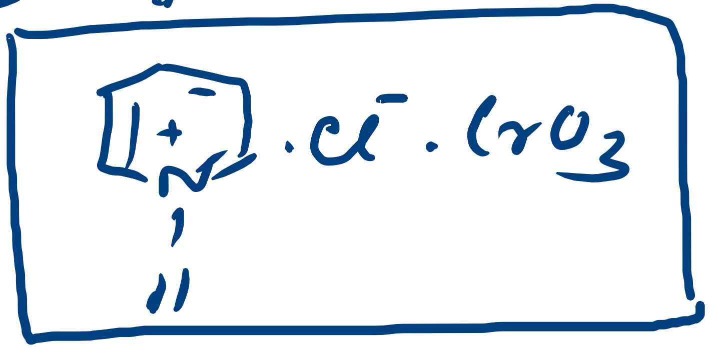
orange green.

MILD OXIDISING REAGENT

M.O.R (Mild oxidising reagents) example:

i) PCC. (Pyridinium chloro chromate.)

 . HCl . CrO_3



ii) ($PCC + CH_2Cl_2$) Collins reagent.

iii) $PCC + CH_2Cl_2$ Sarett's reagent.

iv) PDC. (Pyridinium ~~chlorochromate~~ dichromate.)

v) CrO_3

vi) CrO_3 in glacial acetic acid.

CrO_3.

$CrO_3 + H_2O$

H_2CrO_4

CrO_3

+ conc.

H_2SO_4

SOR

vii) NBS

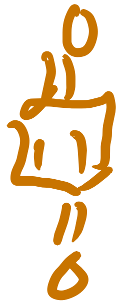
$RCH_2OH \longrightarrow RCH=O$

$R_2CHOH \longrightarrow R_2C=O$

$R_3C-OH \longrightarrow$ no reaction.

viii) Oppenauer Oxidation.

Al-tertiary butoxide

$Al(OCMe_3)_3 + >C=O$ /  solvent

solvent

Special type of oxidising agents.

i) $Cu/300°C$.

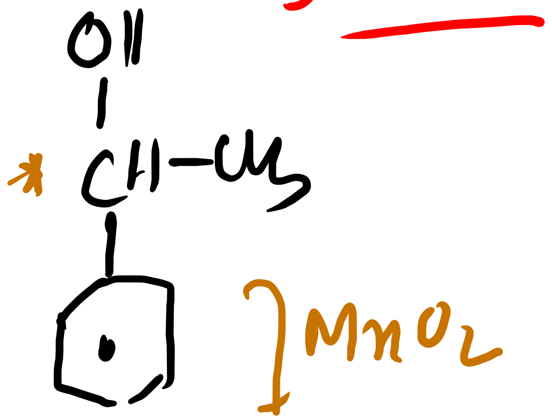
(1° Alcohol) $RCH_2OH \longrightarrow RCH=O$ (dehydrogenation)

(2° Alcohol) $R_2CHOH \longrightarrow R_2C=O$ (dehydrogenation)

(3° Alcohol) $H_3C-\underset{CH_3}{\overset{CH_3}{C}}-OH \xrightarrow{\Delta} (H_3C)_2C=CH_2$ (dehydration)

ii) MnO_2

It oxidises 1° Alcohol (RCH_2OH) & 2° Alcohol (R_2CHOH) to form aldehyde & ketone provided alcoholic $-OH$ group is at allylic / benzylic position.



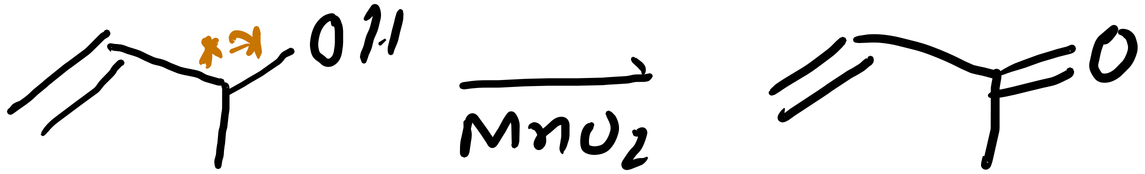
$CH_2=CH-\overset{*\,*}{C}H_2OH \longrightarrow CH_2=CH-\underset{O}{\overset{}{C}}H$

(allylic position)

(benzylic position)

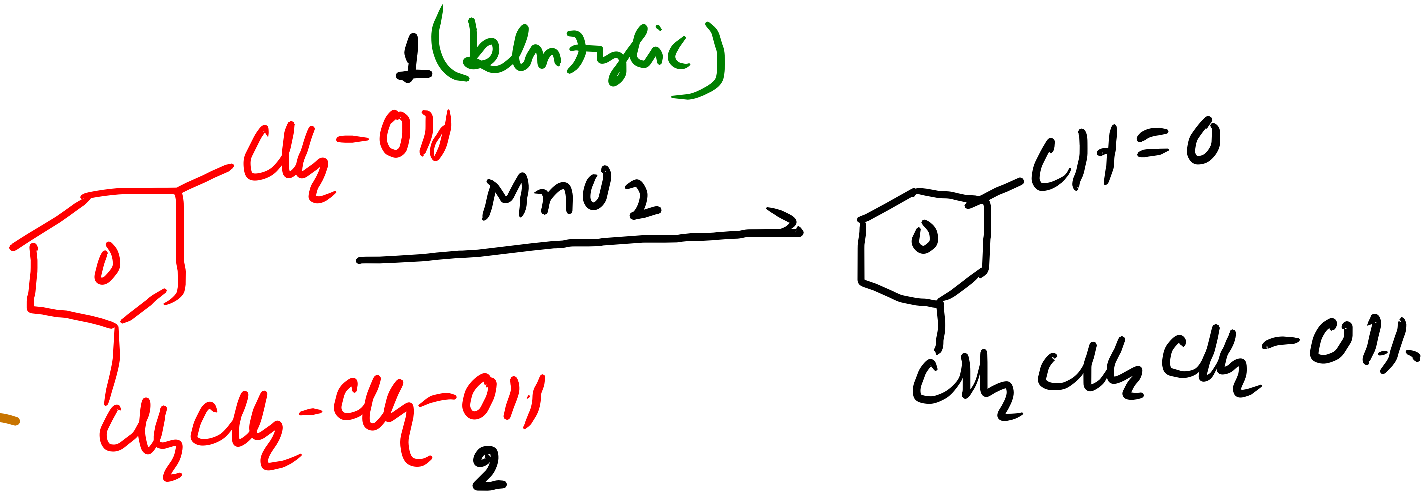
* ⇒ Benzylic position.

** ⇒ allylic position



Reduction - O. I:

Alcohol & chain - O - I:



1 (allylic) ... 2

$HO-CH_2-CH=CH-(CH_2)_5-OH$

$\downarrow MnO_2$

$O=CH-CH=CH-(CH_2)_5-OH$ ✓

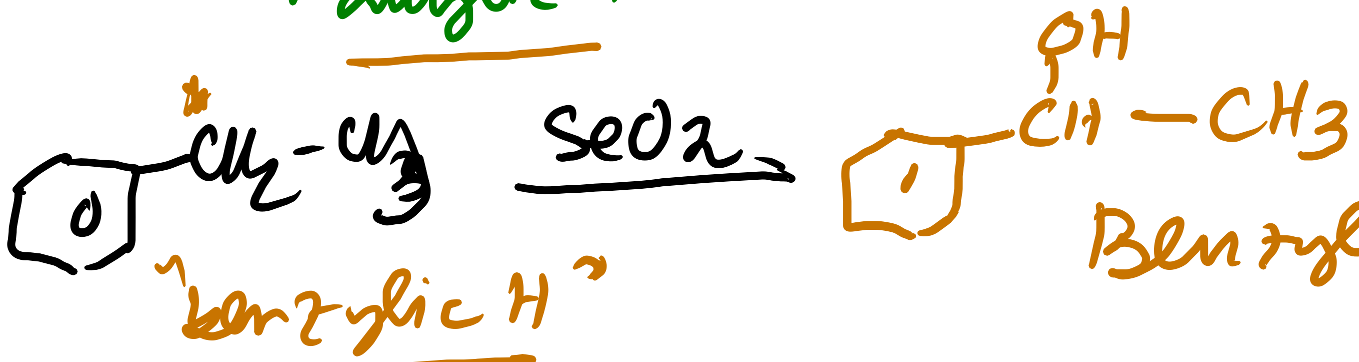
: SeO_2: This is used for alcohol preparation.

Actually it is used to substitute ~~α~~ H at allylic or benzylic position by -OH group.

(I) a) $CH_2=CH-CH_3 \xrightarrow{SeO_2} CH_2=CH-CH_2-OH$

"allylic H" allylic alcohol.

b)



Benzylic alcohol.

(II) ✓Monocarbonyl system ⟶ dicarbonyl system.

$CH_3-\underset{\underset{O}{\|}}{C}-\overset{2\alpha}{CH_3} \xrightarrow{SeO_2} CH_3-\underset{\underset{O}{\|}}{C}-CH=O$

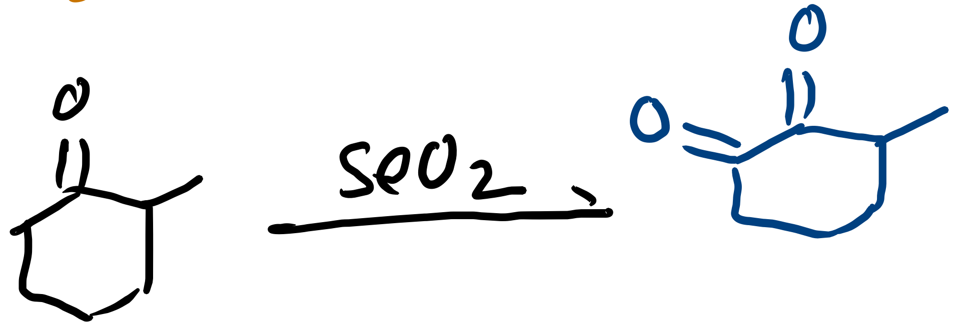
$-\underset{\underset{O}{\|}}{C}-CH_2-$

$\hookrightarrow -\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-$

Total oxidising reagents
8+7+4+3

= 15.

a) $\overset{2\alpha H}{CH_3}-\underset{\underset{O}{\|}}{C}-\overset{\overset{CH_3}{|}}{CH}-CH_3 \xrightarrow{SeO_2} \underset{\underset{O}{\|}}{CH}-\underset{\underset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{CH}-CH_3$

b) 

special oxidising reagents.

(3)
i) Cu/300°C, 3° Alcohol → Alkene.

ii) MnO_2 →
- Allylic 1° → $-CH=O$
- " 2° → $-\underset{\underset{O}{\|}}{C}-$
- Benzylic 1° → $-CH=O$
- Benzylic 2° → $-\underset{\underset{O}{\|}}{C}-$

(4)

iii) SeO_2.

$CH_2=$
- allylic 1°H → allylic 1°OH
- allylic 2°H → allylic 2°OH
- Benzylic 1°H → benzylic 1°OH
- Benzylic 2°H → Benzylic 2°OH.

$R-\underset{\underset{O}{\|}}{C}-CH_3 \rightarrow R-\underset{\underset{O}{\|}}{C}-CH=O$

i) M.O.R

(8).
1. PCC
2. PDC
3. Collins
4. Sarett
5. NBS
6. $Al(OCMe_3)_3$ + 
7. CrO_3
8. CrO_3 + Glacial acetic acid

S.O.R

i) $KMnO_4, H^+$ or OH^-

ii) $K_2Cr_2O_7$, H^+

iii) $CrO_3 + H_2O / H_2CrO_4$

iv) Jones reagent.
$CrO_3 + H^+$ / conc. H_2SO_4

0-1: Halogen derivatives ✓

0-1 Alcohol & Ether } Homework for Saturday.

0-1. Reduction

Aldehyde Oxidation:

It is easy to oxidise aldehyde to form their carboxylic acid.

$$RCH=O \xrightarrow{[O]} R-\underset{\underset{O}{\|}}{C}-OH.$$

But ketone is reluctant to get oxidised.

So the following reagents are used to oxidise aldehyde only but not ketone.

i) Tollens reagent ($AgNO_3 + NH_4OH$; $Ag(NH_3)_2^+$; Ag_2O; silver mirror test)

ii) Fehling solution: (Cu-tartarate solution; [Cu^{2+} (tartarate)]

iii) Benedict Solution: (Cu-citrate solution) [Cu^{2+} (citrate)]].

iv) Schiff's reagent

Tollens (colorless reagent)

$$[Ag(NH_3)_2]^{+1} \xrightarrow{+RCH=O} Ag \text{ mirror} + [R-\overset{O}{\overset{\|}{C}}-OH]$$

aldehyde gets oxidised. salt g

d^{10}

Tollens get reduced

=) aldehyde (all) Aliphatic & Aromatic aldehyde both give +ve tollens test

$RCH=O \longrightarrow RCO_2^-$

$PhCH=O \longrightarrow PhCO_2^-$

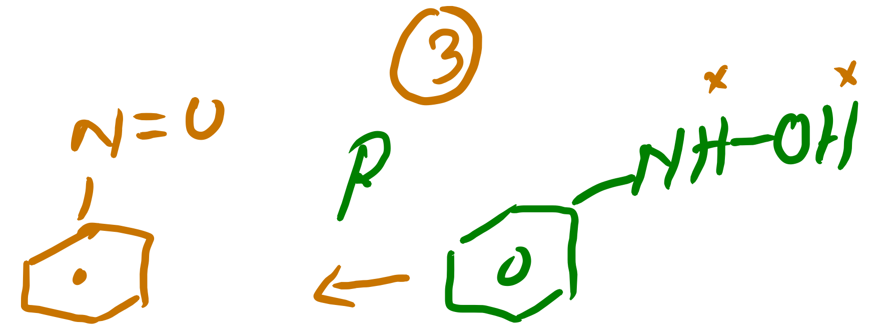
[+ shining silver mirror]

=) $R-\overset{O}{\overset{\|}{C}}-R$ can not give +ve test. because it is difficult to oxidise $R-\overset{O}{\overset{\|}{C}}-R$

:Exception: The folling cpds give +ve Tollens test though it does not have $-CH=O$ group

a) $H-\overset{O}{\overset{\|}{C}}-OH$ [formic acid +ve test, only monocarboxylic acid which give +ve Tollens test]

(b) $R-\overset{O}{\overset{\|}{C}}-\overset{\alpha}{C}H_2OH$ (α hydroxy ketone gives +ve Tollens test) $CH_3-\overset{O}{\overset{\|}{C}}-\underset{OH}{CH}-CH_3$ (+ve test)



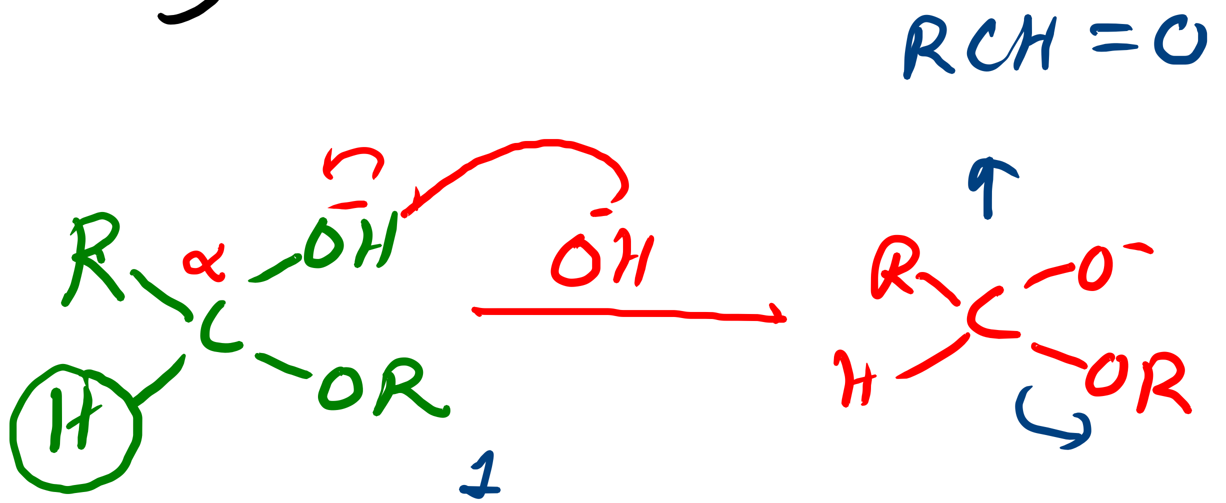
③ : Phenyl Hydroxyl amine

$RNHOH$: Alkyl hydroxyl amine

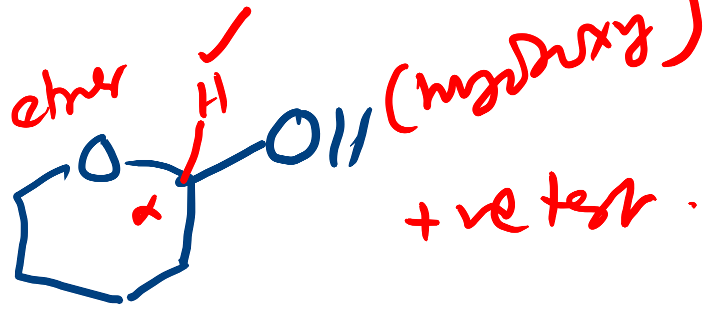
$R-N=O$

These nitrogeneous compounds can give +ve Tollens test.

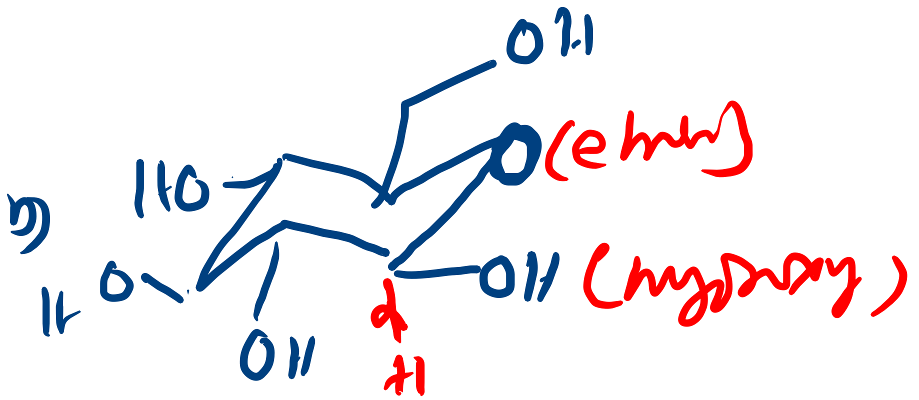
④ Hemiacetal (α hydroxy ether)



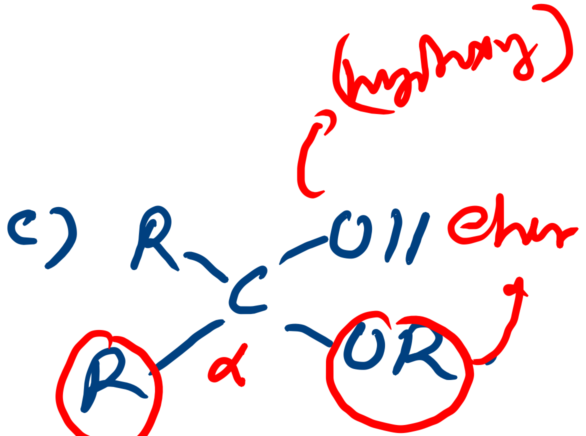
↳ at least α H must present

a) 

+ve test.

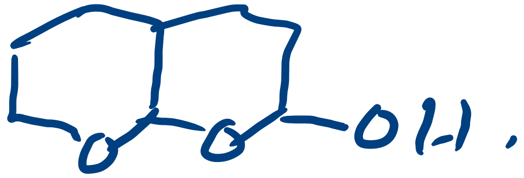
b) 

(+ve test)

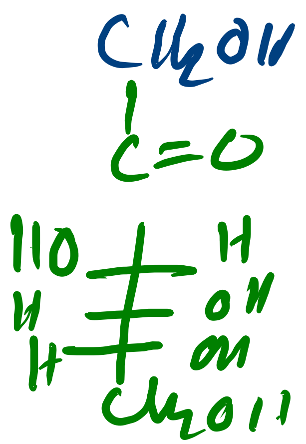
c) 

(no α H)

(+ve test)

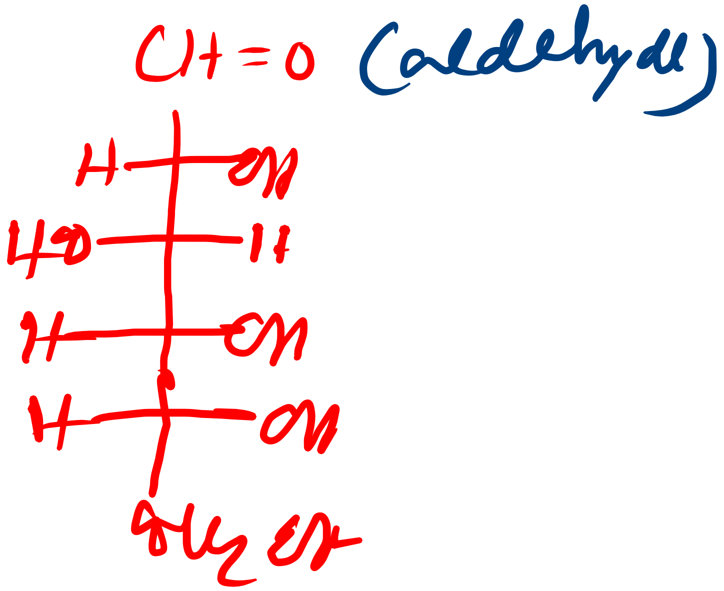
d) 

(+ve test)



{D-fructose}

+ve test



D-glucose

+ve test.

The following compound when reacts with Tollens reagent, it gives white ppt but not giving +ve silver mirror test.

Which cpds gives +ve silver mirror test ?

Ans: Terminal alkyne $RC\equiv CH$ reacts with Tollens but can not give +ve silver mirror test. Instead of silver mirror actually white ppt is formed.

$$HC\equiv CH + 2AgNO_3 + 2NH_4OH \rightarrow \underline{AgC\equiv C\text{-}Ag]} + 2NH_4NO_3 + 2H_2O$$

nonredox reaction:

Ag_2C_2 (silver acetylide) white color ppt.

$$CH_3\text{-}C\equiv CH + AgNO_3 + NH_4OH \rightarrow CH_3C\equiv CAg\downarrow + NH_4NO_3 + H_2O$$

white ppt.

Nonterminal alkyne $CH_3-C\equiv C-CH_3$ (As there is no acidic hydrogen)

↳ (−ve test with Tollens reagent)

$CH_3-CH_2-C\equiv C H^{+1}$ vs $CH_3-C\equiv C-CH_3$ (Distinguish)

(one having acidic hydrogen) (one does not have acidic hydrogen)

$\boxed{AgNO_3 + NH_4OH}$	white ppt. $CH_3CH_2-C\equiv CAg\downarrow$	+ve test	no ppt.	−ve test. due to absence of acidic H.
CH_3MgX	$CH_4\uparrow$	+ve test	−	
NaH^{-1}	$H_2\uparrow$	+ve test	−	
$NaNH_2^{-1}$	$NH_3\uparrow$	+ve test	−	
Na metal	$H_2\uparrow$	+ve test	−	
$Cu_2Cl_2 + NH_4OH$	red color ppt		−	

$HC\equiv CH + Cu_2Cl_2 + 2NH_4OH \longrightarrow CuC\equiv CCu\downarrow$ $+2H_2O$

Cu_2C_2

Cuprous acetylide

(red ppt)