Alkynes
2 - Reactions

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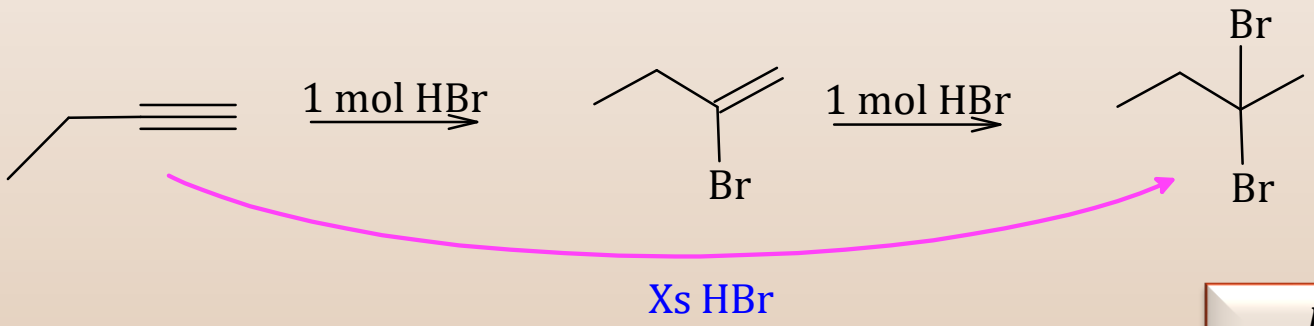
Reactions of Alkynes

Most alkyne reactions are addition reactions, just like alkenes. And since alkynes have twice the hydrogen deficiency index of alkenes so all additions are twice (2 mols) than that of alkenes (1 mol).

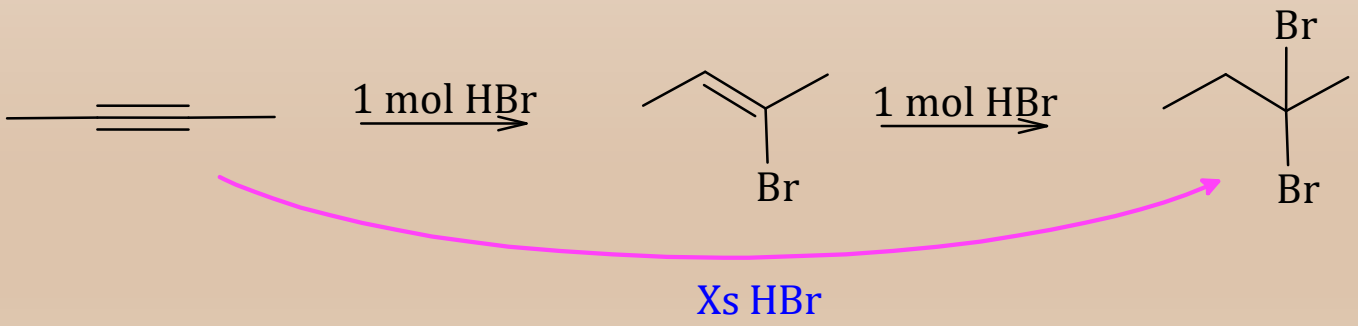
- Another view of alkynes is that they are more oxidized than alkenes (alkynes have less number of hydrogens), so in some reactions alkynes will give the more oxidized product. (Alkenes give alcohols whereas alkynes will give aldehydes).
- Addition Reactions of alkynes are:
  - Hydrohalogenation (HX)
  - Halogenation (X_2)
  - Hydration (H_2O)
  - Hydrogenation (H_2) (reduction)
- Alkynes undergo oxidative cleavage with ozone and potassium permanganate.
- Acidity of alkynes.
- Chain elongation.

Addition of HX

On addition of hydrogen halide (HBr or HCl) is Markovnikov's addition no matter if the alkyne is internal or terminal. (Note: the product is a geminal dibromide)

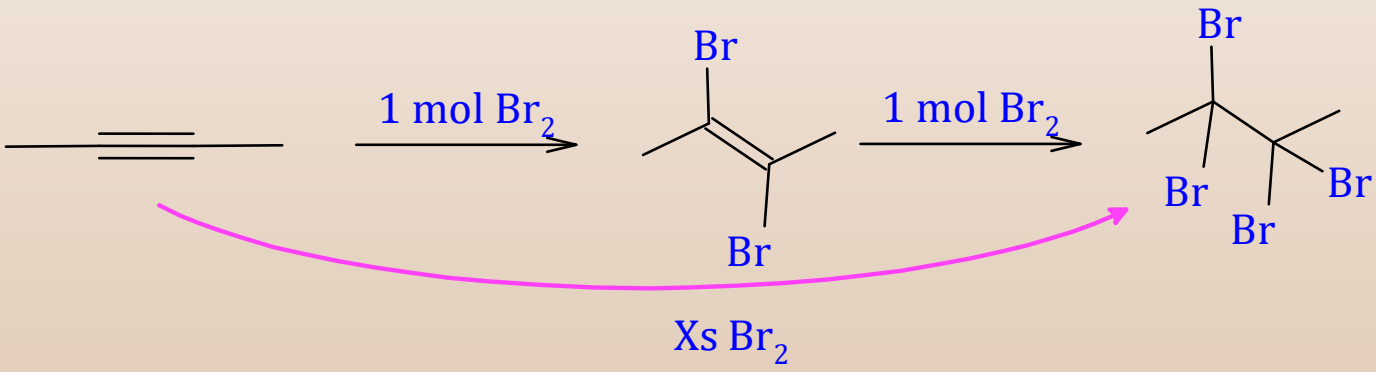


Markovnikov's Product – only product



Addition of Halogen (X_2)

Halogens can be added to alkynes. Usually, the intermediate halogenated alkene cannot be isolated as it reacts further with excess reagent to give the tetrahalide product.

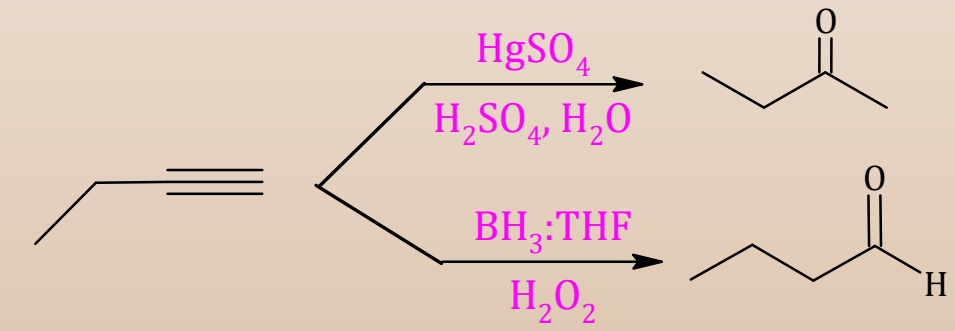


Hydration

Hydration of alkynes give aldehydes and/or ketones depending on the location of the alkyne. Hydration cannot be carried out simply with water and acid catalyst.

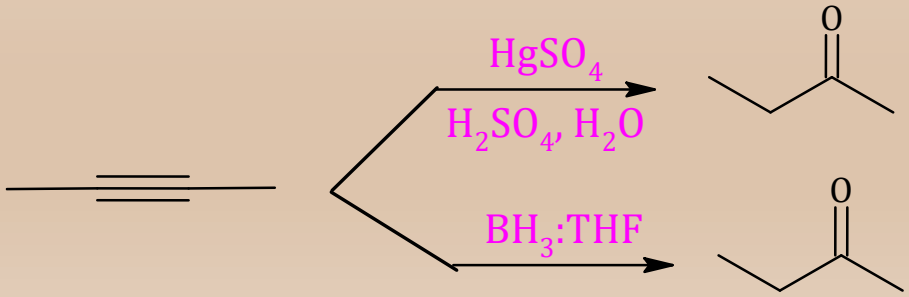
The two reagents used for hydration are:

- $HgSO_4$ in H_2SO_4 to give ketones (Markovnikov's product) for internal and terminal alkyne.
- BH_3:THF and H_2O_2 to give aldehydes (Anti Markovnikov's product) in case of terminal alkynes and give ketones for internal alkynes.



Markovnikov's Product – ketone

Anti Markovnikov's Product – aldehyde

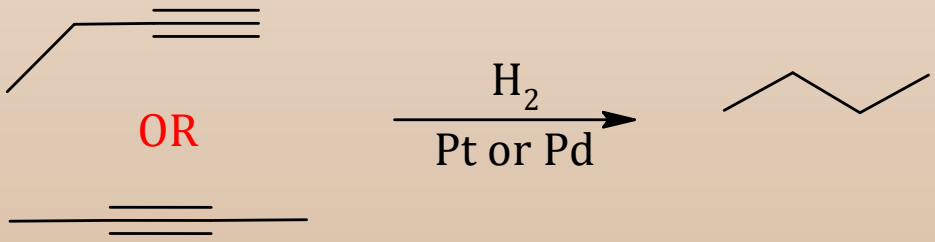


Internal alkynes will give only ketones

Reduction to Form Alkane

There are three reductions that can be carried out with alkynes. One is complete reduction to form alkane, and two different reductions to form the cis and trans alkenes.

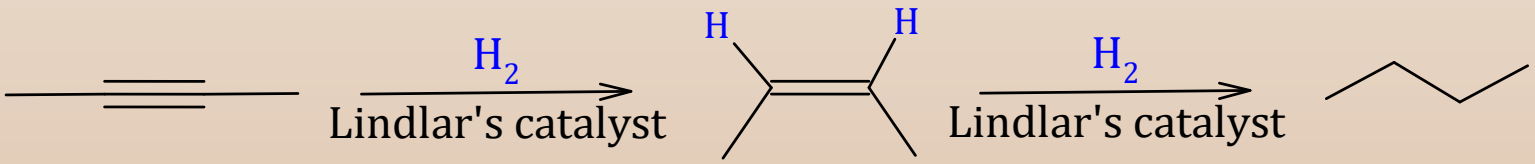
- Addition of H_2 over a metal catalyst (such as palladium on carbon, Pd/C) converts alkynes to alkanes (complete reduction)
- The addition of the first equivalent of H_2 produces an alkene, which is more reactive than the alkyne so the alkene is not isolated.



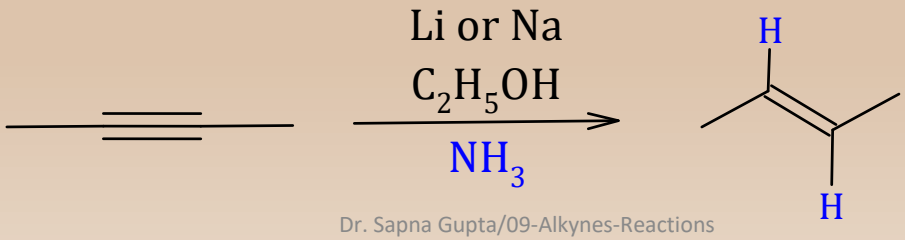
Reduction to Form Alkene

Synthesizing a CIS Alkene: Addition of H_2 using chemically deactivated palladium on calcium carbonate as a catalyst (the *Lindlar catalyst – Pd-$CaCO_3$*) produces a ***cis alkene.***

The two hydrogens add ***SYN*** (from the same side of the triple bond). The mechanism is similar to hydrogenation covered in alkenes where hydrogen is adsorbed on the metal and the alkene is in the correct orientation with the hydrogen to form a cis alkene. Only one mol of hydrogen is added at one time.

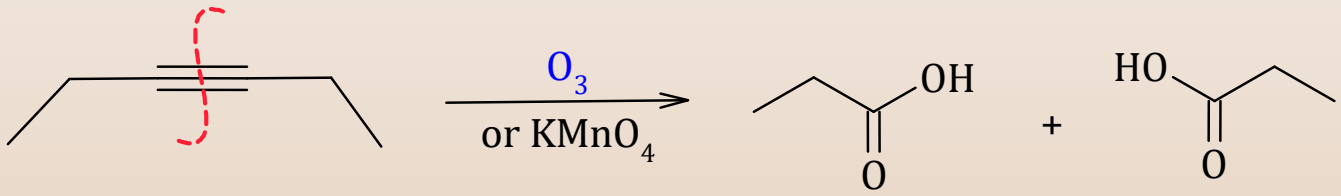


Synthesizing a TRANS Alkene: Alkali metals dissolve in liquid ammonia (below –33 ºC) also function as reducing agents. Alkynes are reduced to form ***trans*** alkenes with sodium or lithium in liquid ammonia. This is ***ANTI*** addition.

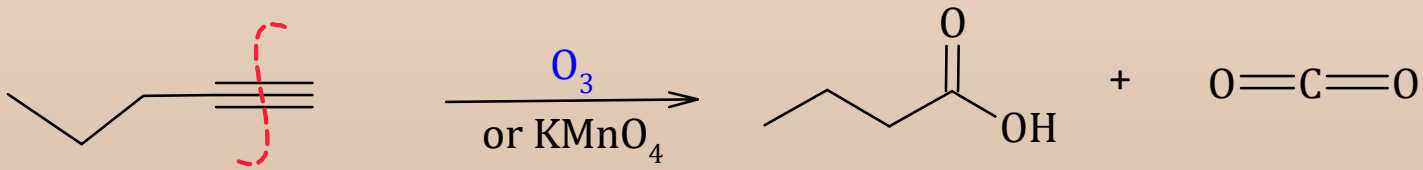


Oxidative Cleavage

Alkynes will give cleave into carboxylic acids during oxidative cleavage with oxidizing reagents (O_3 or $KMnO_4$).

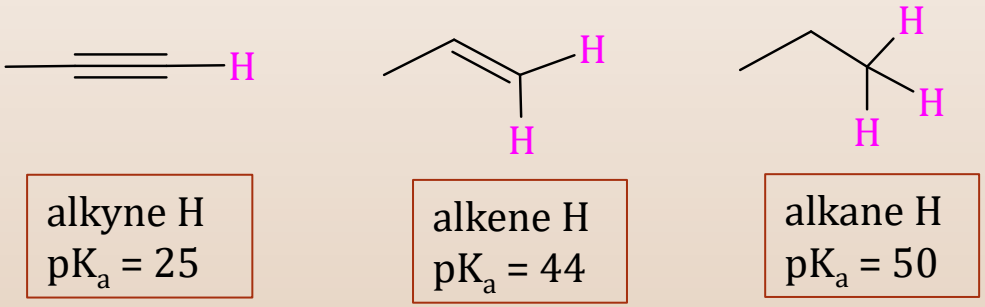


- Terminal alkynes are oxidized to a carboxylic acid and carbon dioxide

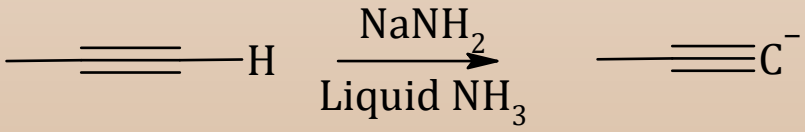


Acidity of Alkynes

We learned in acids and bases that alkynes are strongest acids amongst the hydrocarbons. (alkynes> alkenes > alkanes), as also shown by the pKa values below.



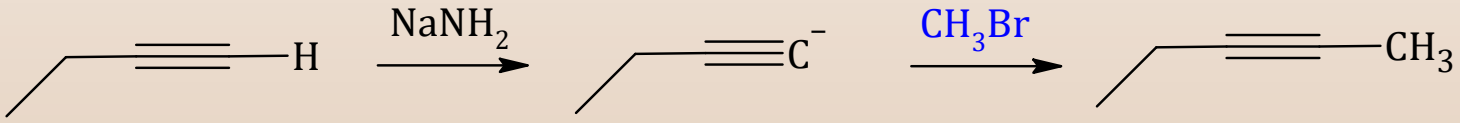
- Since the pKa is relatively high, only a strong base like amide, NH_2^-, can be used to abstract the alkyne proton to give the alkynide anion (the conjugate base).



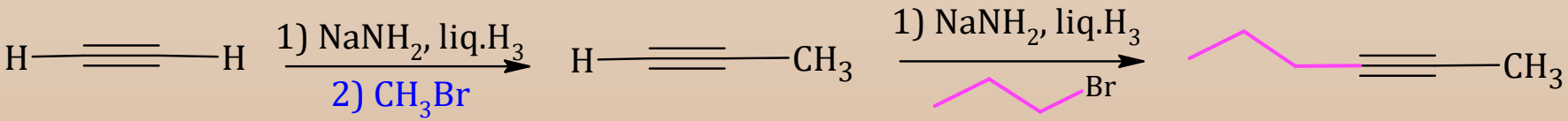
- The alkynide ion can then be used as a nucleophile for any substrate (that has a leaving group).
- Depending on the substrate substitution or elimination can occur.

Chain Elongation

The alkynide ion formed from the treatment of a terminal alkyne with a strong base can be used as a nucleophile. When added to a primary alkyl halide substrate, a S_N2 reaction can occur. This reaction is also called chain elongation, since the alkyne is still there but a carbon or a carbon chain has been added.

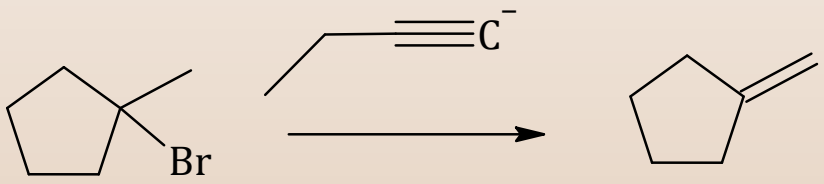


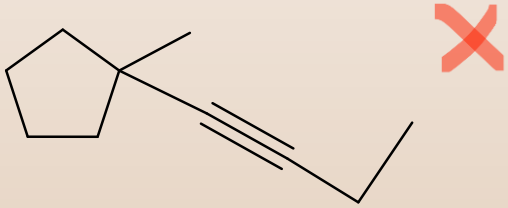
- If there are two acidic hydrogens, e.g., in ethyne, then this reaction can be repeated to extend the chain on either side of the triple bond.



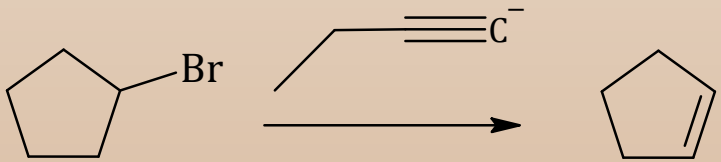
Alkynes as Bases

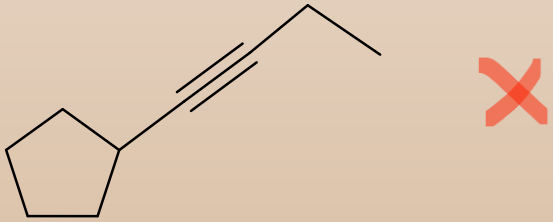
Reactions with 2º and 3º alkyl halides gives dehydrohalogenation, converting alkyl halide to alkene. This happens because the alkynide is a bulky base and ends up giving the Hoffman product in an E2 mechanism.





S_N2 will not happen





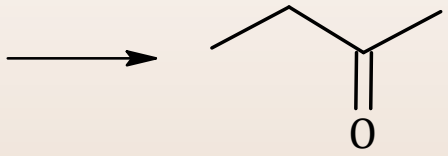
S_N2 will not happen

Solved Problem: Reactions of alkynes

Show how you will make the ketone below using a) an alkyne and b) an alkene.

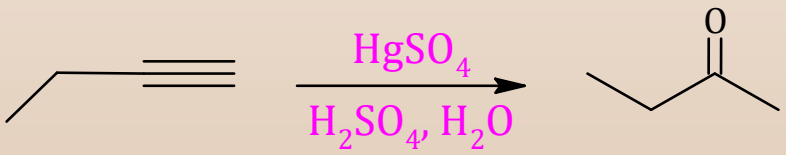
an alkyne

an alkene



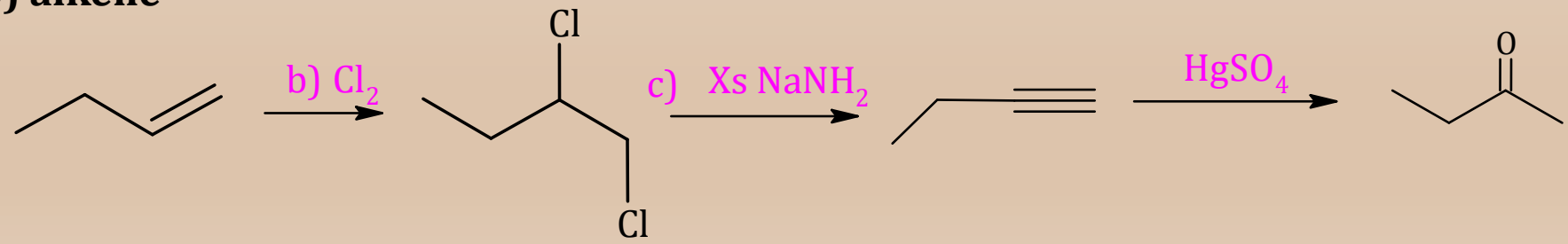
ANSWER

a) alkyne



Answer

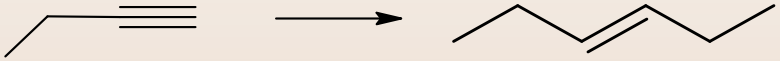
b) alkene



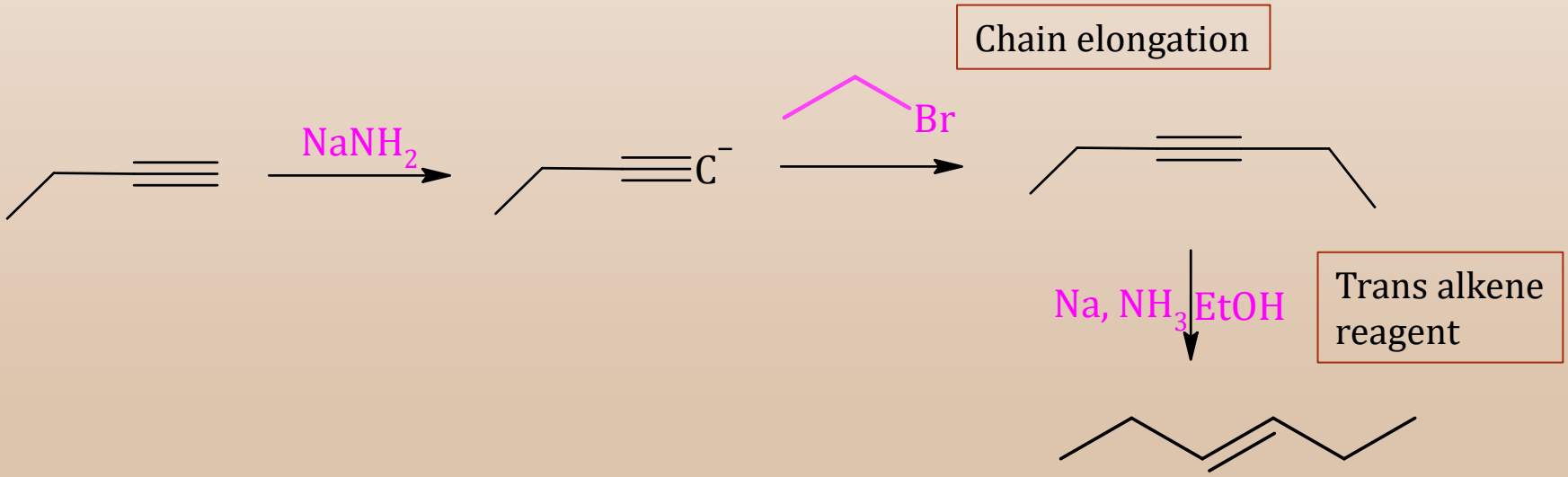
Solved Problem: Reactions of alkynes

Show how you will make trans hexe-3-ene from but-1-yne.

ANSWER

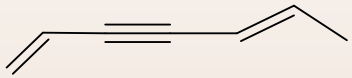


Notes: There are added carbons in the product, so C-C bond formation, which is by **chain elongation**. A reaction has to be done on alkyne to make the **trans** alkene.

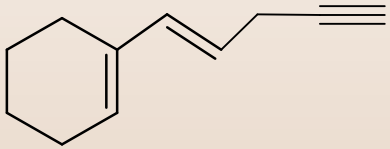


Solved Problem: Reactions of alkynes

a) What are products obtained from ozonolysis of the following compound.

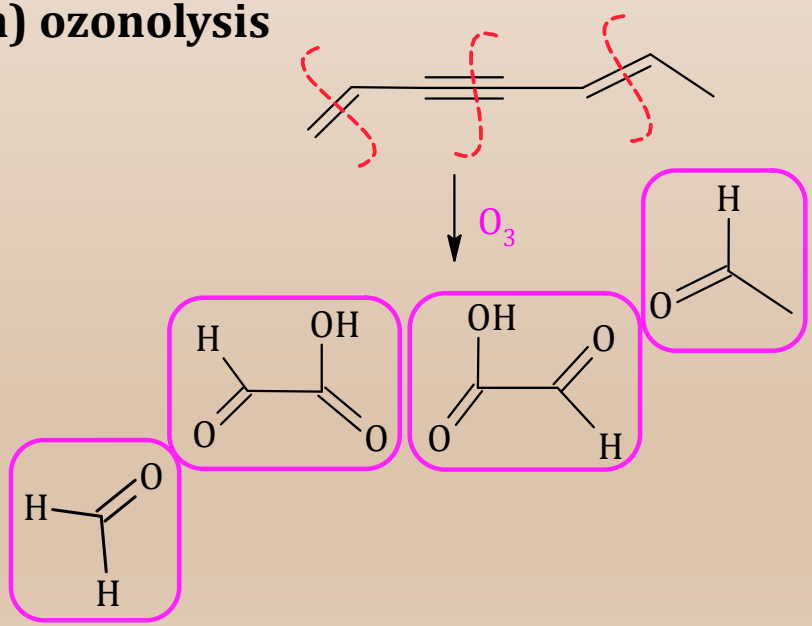


b) How many carbon dioxide molecules and carboxylic acid functional groups will be made on treatment of the following compound with potassium permanganate.



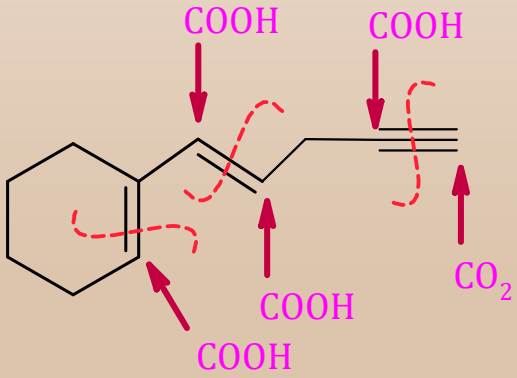
ANSWER

a) ozonolysis



ANSWER

b) $KMnO_4$ – 4 carboxylic groups and one CO_2.



Qualitative Analysis

- Alkynes are very similar to alkenes in reactions, so the qualitative tests are the same (i.e. decolorization of bromine and brown ppt of MnO_2)
- However, since alkynes have twice the hydrogen deficiency of alkenes, one can do a quantitative test along with qualitative test; an alkyne will react with twice the amount of bromine as an alkene would. So simply counting the number of bromine drops until the color stays will give an idea of whether there is an alkyne or alkene.
- But – that is also not a determinant if you have no idea what groups you are starting with because a dialkene will react with the same amount of bromine as one alkyne!

Key Words/Concepts

- Addition reactions
  - Halogenation
  - Hydrohalogenation
  - Hydration
  - Hydrogenation (cis and trans)
  - Chain elongation
- Oxidative cleavage