

myself punya murthy from iit gawhati i welcome you to iit paal program in this class we will study about all kinds alkynes are hydrocarbons that contain at least one carbon carbon triple bond example ethane and they have general formula  $C_n H_{2n-2}$  in the previous classes we have seen about alkanes alkenes this is saturated hydrocarbon and if you look at this one they have general formula  $C_n H_{2n+2}$  next we have seen about alkenes they are also unsaturated hydrocarbons and it has they have at least one carbon-carbon double bond they have general formula  $C_n H_{2n}$  and if you compare these three hydrocarbons alkanes have less number of hydrogen atoms for example in this case you have two carbon six hydrogen atoms in this case you have four hydrogen atoms here only you have the two hydrogen atoms they have general formula  $C_n H_{2n-2}$

So let us see the structure of the carbon carbon triple bond if you look at the orbital structure of this molecule

So this each carbon and this has two sp hybrid orbital which involve the bond formation and the overlapping of one sp orbital of this carbon with another sp hybrid orbital of this carbon leads the formation of the sigma bond

So out of the two sp hybridized orbital one is involved the formation of carbon carbon bond the remaining sp hybridized orbital overlaps with this s orbital of hydrogen to form the carbon hydrogen sigma bond similarly this sp hybridized orbital of this carbon can overlap with this hydrogen s orbital of hydrogen to form this carbon hydrogen sigma bond there are two unhybridized p orbital and the one of this p orbital of this carbon for example this one the unhybridized p orbital can overlap with the p orbital of this carbon and these two orbitals parallel and they can overlap side on approach they can form the carbon carbon pi bond

So overlapping of these two p orbitals and hybridized p orbitals results the formation of this pi bond there is one more unhybridized p orbital that is perpendicular to this orbital

So this carbon carbon carbon hydrogen sigma bond all on the linear molecule and perpendicular to that you have the p orbital they overlap then they make the result the formation of the pi bond perpendicular to that p orbital you have another p orbital

So this can overlap with this orbital this orbital can overlap with this one

So if you look at this one this is perpendicular to that 90 degree between these two orbitals they can make another pi bond

So if you look at this one it has three sigma bonds one carbon carbon sigma bond you have one carbon carbon sigma bond and two carbon hydrogen sigma bond in addition to that you have two pi bonds these pi bonds are formed by the overlapping of these two unhybridized p orbitals

So if you look at it is like cylindrical right you have the top and bottom you have the pi electron cloud similarly this pi electron cloud and like completely this molecule and around that there is a pi electron cloud that makes this molecule as linear we see the bond angle between this carbon carbon bond and ch bond is 180 degree the bond length is one point two armstrong the shorter than carbon carbon double bond

carbon-carbon single bond and this bond length is 1.09 armstrong this is a structure of all kind and we have taken ethane an example we have seen the structure and it involves the sp hybrid orbital of carbon overlaps with s orbital hydrogen to give to form the carbon hydrogen sigma bond and similarly this sp hybrid orbital of this carbon overlaps with this carbon sp hybridized orbital and head on approach to form the sigma bond now let us look at the nomenclature and isomerism of alkynes in the iupac system the names of alkynes are derived from the corresponding alkanes by replacing the suffix a and e with y and e for examples the corresponding alkane is ethane this is iupac name of this molecule is ethyne is this the first member of this alkyne series iupac name of this alkyne is ethane the corresponding alkane is ethane if you look at it the suffix a and e has been replaced by y and e let us look at the next example

So iupac name of this alkane is propane the corresponding alkene is propene

So the first two members of this series have only one structure ethane propene ethene propene and ethane propane when you go for next member butane there are two structures possible in the case of butane you can look at this one and this is called 1-butyne and 2-butyne this iupac name of this compounds and this one and two refers the position of the triple bond present in this molecule when you go for the next molecule having molecular formula  $C_5H_8$  there are three possible structures there are three possible structures

So so these two compounds differ their position of the double bonds

So name of this compound is pent-2-yne and this one is pent-1-yne and this

compound three methyl one butane

So if you see these structures these two are uh this posterior isomers if you see here the carbon carbon triple bond present under different positions in this case present between the carbon 1 and 2 here between the carbon c 2 and 3 therefore this relationship between these two compounds are called positional isomers and similarly in this case the double bond the triple one present between this carbon one and two here two and three these two are called positional isomers and if you uh compare these two compounds this a linear is a transit one the relationship between these two compounds is chain isomers similarly between this and this chain isomers because this is a linear is a branched one this about the isomerism they can have they have all look at it they have same molecular formula but different structures

So these are linear structures and

So they differ in the position of the triple bond then they are called positional isomers but when you compare with this one then they are called chain isomers this is a branched one this is a linear one

So next let us look at the preparation of alkynes there are two common methods are used to prepare alkynes and the first approach uh the is the reaction of calcium chloride with water when you react when you treat calcium carbide with water it can give a oscillating ethene this industry uses to prepare ethine by using this method because this one of the important alkynes in the because we widely use for us ethan to make new organic compounds as well as to make materials and this very important industrial process when we treat calcium carbide with water it can give austerlin and this ethen asylum is a common name and this is a solid compound say solid compound solid compound when you treat with water you can generate ethane as gas and calcium carbide is produced from calcium carbonate when you heat calcium carbonate it can produce calcium oxide plus carbon dioxide when you react calcium oxide with the carbon you generate calcium carbide and carbon monoxide here ah involves two molecule of water

So you can generate ah you can ah this is the reaction is involved calcium carbonate is when you heat it produces calcium oxide and this calcium oxide when you react with carbon you generate the calcium carbide this when you treat with water you can produce ethane gas

So how industry uses to prepare ethane the next uh approach common approach to prepare ethan is um dehydro dehalogenation reactions for example if you have for example this one die hello compound

So this when you treat this one to dibromo alkane with alcoholic a wh is a base

So it can remove this hydrogen this is a base it can remove one of the hydrogen for example if you remove this hydrogen you generate let us write like this the base can remove proton

So in this case the base will remove this proton you generate the alkenyl bromide are called vinyl bromide intermediate once you form this one you have to further react with a strong base this you produce this alkene plus potassium bromide plus water this will be the byproduct in this reactions and

So once you form this one the potassium the hydroxide the alcoholic k which is not sufficient enough to remove this proton right now you have to remove this proton

So you have to use strong base like sodomide and this can ah this now ns2 this is the base this can remove proton another dehydrator halogenation you can product basically it involves two steps first what you have to do in this the byte product is going to be sodium bromide plus ammonia

So first the algal here which removes one of the ah proton it's actually base you do dehydro halogenation and further you have to use strong base to remove proton from this alkenyl bromide then you can convert into alkyne this is another process we use to make alkynes

So far we have seen the structure of carbon-carbon triple bond then normal culture isomerism then preparation of alkynes we have seen two approaches one is how you can industry prepares heat and gas using from calcium carbonate calcium carbonate when you heat and it it it gives carbon calcium oxide the calcium oxide can be reacted with the car ah carbon as a carbon to give calcium carbide that causing carbide when you treat with water it can produce ethane gas and the next we have seen if you have a vicinal dihalo compound you can treat with base first alcoholic koh you can convert into vinyl halide that can be further reacted with a strong base then you can get the alkyne next physical properties of alkyne as we have seen in the previous classes about alkanes and

alkenes the first three members of the series ethane propene butane they are gas the next eight members  $C_{12}$   $C_{13}$   $C_{14}$   $C_{15}$   $C_{16}$   $C_{17}$   $C_{18}$   $C_{19}$   $C_{20}$  they are liquid

So next eight members are liquid compounds after that all are solid compounds higher molecular alkynes they are solid compounds they are colorless as alkanes and alkenes colorless except ethane it gives a garlic odor and the remaining are waterless the density of alkanes as we have seen earlier alkenes they are less than a water less than one

So they uh they they also they are less polar compounds they don't mix with water very well but however they are well soluble in organic solvents and if you look at the melting point and boiling point density

So when you increase the molecular weight these also increase as we have seen the case of alkane and alkenes if the homologous compounds and if you compare with alkene and alkanes show high boiling and melting points because they are linear molecule they can stack each other very easily comparing to alkenes because of that they show high boiling and melting points

So now let us look at the chemical properties of alkynes first let us look at ethane just we have discussed the  $sp$  hybrid orbital of carbon is involved the sigma bond formation between with this carbon and as well as with the hydrogen in this case if you look at this one the  $sp^2$  hybrid  $sp$  hybridized orbital carbon overlaps with this  $s$  orbital of hydrogen and to form the carbon hydrogen sigma bond

So if you look at this this one the  $s$  character is increased if you see the alkane it involves  $sp^3$  hybrid orbital the  $C-H$  bond formation in the case of alkene  $sp^2$  is involved here  $sp$  orbital hybrid orbital is involved in the carbon hydrogen sigma bond formation So the  $s$  character is here 50 percent that means the electron density the electron whichever involved the bond formation is very close to the carbon and the electro in other words the electronegativity of this carbon increases because of the  $s$  character is more in this carbon and

So the base can easily remove the hydrogen as proton when you treat with base for example when you treat with a sodium liquid ammonia it can easily remove this proton it can produce sodium acetylide and similarly and this also it can further react another sodium and it can produce similarly this also we can react with soda amide this of course you can react with alkyl halide then you can couple this moiety and this is very very useful reaction

So this if you compare the acidity of alkynes with alkenes and alkanes they follow the order this is more acidic just like I have told you and this involves the due to the  $sp$  character the electronegativity of this increases and the base can easily remove the hydrogen as a proton and this more acidic and this is less acidic comparing to the alkyne however more acidic comparing to alkane this least acidic among all the three hydrocarbons these two are saturated unsaturated saturated hydrocarbons

So if you compare between different alkynes and this will be more acidic comparing to this because you have the methyl group it can give electron to this system and if you go further this will be the least acidic this is the more acidic comparing to this this more acidic comparing to that this acidity of acidity order of all kinds

So now let us look at some of the important reactions addition of hydrogen alkynes can readily undergo reaction with hydrogen in the presence of catalyst like palladium platinum nickel it can undergo addition to give alkene the alkene can be further reduced into alkane

So depends upon the catalytic system suppose if you take alkyne and in the presence of hydrogen if you use palladium catalyst a straight away it can be reduced into alkane first it is converted into alkene that alkene undergoes further reduction to alkane if you remember the first class I have shown you what happens you see this hydrogen adsorb on the surface of the finally divided the metal surface and then your alkyne also adsorb it makes  $\pi$  bond interaction can with the metal can interact and once it is observed on the surface then the hydrogen transferred to the alkyne and then you you get alkyl metal intermediate that can be further reacted with another hydrogen you get the alkene then in this way the alkene can be further converted into alkane and

So if you use on the other hand you can also stop the reaction at this stage and if you use a linear catalyst the presence of quinoline and what happens the activity of this catalyst less as soon as you form the alkene it cannot reduce further alkene to alkane So depends upon the reaction conditions

So you want to have alkene or alkane both can be obtained from alkyne and using the catalytic hydrogenation reactions where the hydrogen adds the same side of the carbon-carbon triple bond is in addition the reaction stereo specific we have seen during the discussion on the alkenes as well as alkanes and also alkenes can all alkynes can also be reduced to alkenes with the trans uh stereochemistry using sodium liquid ammonia this we have seen during the reaction of the preparation of trans alkenes the next reaction is

So addition with halogen alkynes readily undergo a reaction with the halogen it can when you treat for example with the bromine it can undergo addition with this carbon carbon triple bond you can form the one two dibromo ethene ah

So in this case the vicinal both carbons have bonded with this bromine this addition reaction is electrophilic addition reaction and just we have seen the last class it undergoes addition you make prominent intermediate then it attacks you get this diode to dibromo compound this can also further undergo reaction with another bromine and you can have tetra bromoethane you can make this compound and this this involves electrophilic addition reaction the addition of hydrogen halide the mechanics is similar to whatever we have seen yesterday to alkenes and in the case of hydrogen halide let us take propanus example when you treat propane with hydrogen hydrogen bromide it can produce ah two two thai bromo ah propane in this case if the reaction goes by a margonico product what happens first one of the hbr reacts first the formation of vinyl bromide takes place once you form this one this can further undergo reaction with another hbr vr minus this can react with this carbocation to give if you look at this this is called geminal dibromide and if you have the adjacent carbon atoms this called visional bromide vicinal dibromide So just we first we have seen the addition of hydrogen then we have seen the halogen where you can introduce you can make tetra halo compound and next what we have seen addition of hydrogen halide using this method you can make a geminal dihalo compound and both halogen under this reaction takes place by a marginal addition the next example is addition of water as we have seen ah the last class this alkene also can undergo addition with water can give a carbonyl compound ah let us take this as example propane when you react with a water it can undergo addition reaction when you heat around 50 to 60 degree celsius the water undergoes addition as we have seen just now from this intermediate which is not stable it can isomerize into ketone osteo

So alkane ah depends upon the alkyne if terminal alkyne it can be in this case it can be converted into ah a stone suppose if you take ethane you do hydration you will get acetaldehyde this very important reaction

So in the presence of hso4 and sulfuric acid and alkane can undergo addition with water the to give this inner form which can isomerize to give the carbonyl compound the next example is osnolysis

So alkane can undergo reaction with ozone for example ah if you treat react this compound with the ozone it can undergo a reaction with the ozone to give ozonide this was annoyed when you react with water let us take um two butane you can you can ah get this osonide intermediate this when you react with the water it can undergo cleavage to give this diketone

So this of course when you treat with a different reagent for oxidation hydrogen peroxide can be further converted into carboxylic acid therefore if you have the alkyne alkane ah can react with ozone to give the ozonite that can be further reacted with water to get the one to die carbonyl compound this also very useful reaction synthetic chemistry the last example is polymerization reaction

So two kinds of polymerization reactions are possible with alkyne and one is a linear for example austeline undergo polymerization and certain conditions to give the polymer this is a general formula if you look at it they are a conjugated system you have the double bond single bond double bond like this therefore the the good conductors and we can use these are less weight comparing to metals and they use as good conductors this is an example for linear polymers and also they can react to give cyclic compound for example when you ah react together to give benzene this very important example to convert aliphatic compound to aromatic compound for example if you take this alkyne when you um around 600 degree celsius they can undergo trimerization to give benzene this very useful reaction to make benzene derivatives and to make the corresponding compounds which is useful in dyes and other application parts and instead of simple ethane you can also use for example propane suppose if we heat this compound they can also undergo trimerization under these conditions to give this trimethyl substituted benzene is very useful

reactions

So let us summarize whatever you have studied today

So first we have seen the structure of carbon carbon triple bond the nomenclature isomerism then we have seen the preparation of all kinds physical properties than chemical properties in the chemical properties we have seen the acidity of all kinds then we have seen some common reactions for example and alkyne can be reduced into alkenes or alkanes and the reaction stereochemistry is specific if you want to make cis alkene you can do catalytic hydrogenation and using palladium lindler catalyst you can make a cis alkene if you want to make trans alkene you can use sodium liquid ammonia yesterday we have the last class we have discussed about the mechanism it goes via single electron transfer reactions and other hand if you use like finely divided palladium platinum nickel based catalyst the hydrogen can further react under addition with alkene ah that catalyst more effective comparing the linear catalyst the alkyne can be directly reduced into alkanes next we have seen the addition of halogen and alkane can undergo a reaction with the two molecules of halogen can give the tetra halo compound and it can also undergo reaction with hydrogen halide for example hbr it goes by electrophilic addition reaction and it follows the markovnikov rule you can get geminal dihalo compound for example if you add hydrogen bromide you can get both you can add both bromine atoms and the same carbon atom for example if you take propane you can get 2,2 dibromo propane it's a very useful reaction then we have seen hydration it can also like that reaction with hydrogen halide it can also undergo addition with the water is also electrophilic addition reaction it follows a markovnikov rule and you can convert into carbonyl compound and it depends on the substrate you can get aldehyde or ketone this reaction is usually carried out at moderate temperature then we have seen ozonolysis you can also convert alkyne to dicarbonyl compound and you can ah it the alkane undergo addition with ozone you form the ozonide that can be further reacted with the appropriate reagent to get the respective compound and for example if you treat with water you get the dihalo die carbonyl compound and if you use hydrogen peroxide it can be further cleaved into get to get a dicarboxylic acids and the last part of the lecture we have seen and this uh the ethane is very important uh compound to make new organic compounds and materials and we see this is industry uh produces ethane from from the reaction of calcium oxide and carbon uh So the calcium oxide can react with uh carbon to generate calcium carbide that calcium carbide when you treat with water it can give the ethane gas and this is a very important start precursor for various organic compounds and this for example it can you can make linear uh polymerization it can give the conjugated polymers which is very good uh conductor uh widely used for various applications and you can also this is a weight the light it has they have light weight comparing to the metals and then we have seen also they can also undergo trimerization to give benzene and the related compounds which also very important in dyes and other aromatic compounds in pharmaceutical industries with this i conclude my lecture thank you very much you