hello everyone i welcome you all
in the series of lectures on ah biomolecules today ah we are going to
start lecture six before going to the main you know discussion on ah lecture
six
i would like to give a recap of last class ah in the last class ah we have
discussed about
ah epimerization epimerization and in dial rearrangement and oxidation reduction
reactions of reactions of monosaccharides moving ahead with the you know ah
carbohydrate
topic today we will discuss about the lengthening of chains in the
carbohydrate lengthening lengthening the chain and for lengthening the chain we
can utilize kiliani fisher synthesis
so we will also i mean discuss about the process by which we can
achieve this lengthening which is known as kiliani fixture synthesis
so how in any sugar molecule if you want
to introduce one more carbon how can you with the required framework how you
can
lengthen that chain i am talking about the poly hydroxy ah carbon chain how
one can
lengthen it how how this transformation can be achieved and as i mentioned
that this
transformation can be achieved from a ah starting material which will be sugar
and ah by
ah applying the kaliani fischer synthesis on it ah and through that what
happens that one carbon
ah increase with the hydroxyl group ah can take place ah in the scaffold
so let us talk about
the kalyani feature synthesis here i am going to start with erythrose as a
starting material
for this reaction
so i am writing first erythrose it throws structure is well
familiar with all of you
so here you can see that erythros is having four carbons and out of four
carbons two carbon are asymmetric
so how we can you know increase one carbon over
here for increasing one carbon i am going to react it with the cyanide ion you
can see here
it throws this hype it throws is basically aldos and it has aldehyde group at
one terminal and
what am i going to do that i am going to react it with the you know cyanide
group that cyanide
can be achieved from the sodium cyanide are from potassium cyanide any cyanide
source ah which can
easily generate the cyanide ion in the reaction mixture under acidic condition
i am reacting
it and for acidic condition i am taking here hcl now you can see here that
this aldehyde
group is sp2 hybridized
so it is having it is pro chiral and it has two faces one is
the top face and other is the bottom face
so two possibility exist here that if it reacts
from the top face and if it reacts from the bottom face
so first we are going to react
it from the top face

so that will give corresponding cyanohydrin now the point to remember here is this pro
chiral carbon will generate another chiral center similarly if it reacts from the bottom face then we will get the another stereoisomer with opposite stereochemistry at the
alpha carbon to the aldehyde group all right
so once this reaction is done we will
reduce it this nitrile group to the reduction of nitrile group for the both the stereoisomers
so for reducing
as we know that we can use hydrogen and palladium bso4 palladium absorbed on bso4 that will generate from nitrile to this will do partial
reduction of this nitrile and that will l generate mean nitrile to ldamine points remember
if we will do we will not do selective reduction then it can nitrile can convert to the amine alkyl
amine however if we use this you know controlled ah reduction where we can use palladium
bso4 and hydrogen it will convert it into ldmin and rest of the scaffold will remain same without any change once we receive similarly for the another stereoisomer we will get we will get reduction of nitrile to ld mean here also we are using same reduction ah reagent now what will i do that for regenerating the aldehyde group on this ld mean i will do acid hydrolysis
so this will be further processed
for acid hydrolysis in presence of hcl and it will regenerate the aldehyde group and for the other isomer also stereoisomer we will get aldehyde
so this molecule is and side product will be ammonium salt in both the cases and counter iron can be chloride over here this ammonium amino chloride will generate as a
so we started with d throws and we we got d ribose and its another disturber what is change over
here we saw that through this protocol we are increasing one carbon and one carbon in the
scaffold in both the diastoma in total it is taking place and ah this is the its a basically
epimer c two e p mar ah basically you know ah the c two e primer of e p mers basically you know its
generates pair of c two pimmers cleoni fischer synthesis leads to a pair of c2 pimmers what is the difference over here you you can see that at the second position the stereo
chemistry is different starting material is same for the both the distromer ok
so again i
will like to you know rephrase the whole clinic fischer synthesis ah in the first step
hydrogen cyanide are you know sodium cyanide or potassium cyanide any source of cyanide adds
to the carbonyl group and this reaction converts the carbonyl carbon in the starting material to an
asymmetric center as i mentioned that this is the asymmetric center you are creating already the
chiral ah two chiral centers are there
so this this transformation is diastole selective and two
stereo centers ah one ah new stereo center forms in the both the diastromer consequently two

products forms are only different at the c2 position this position you know only they are
different if you see in both these cases this positions they are different and the cyanide group
is further getting reduced partially you know parcel reduction not the complete direction by the
deactivated palladium catalyst this is deactivated if it is not that much active deactivated
deactivated palladium catalyst palladium on bso4 you would have seen that generally for the
reduction purposes we use ah palladium on charcoal ah which is quite reactive but here we are using
you know slightly deactivated palladium catalyst and
so that it can lead to the immune
formation here we are forming amine this ld mean is forming element is forming and which is not getting further reduced to the you know corresponding alkyl amine
that that has been done intensely and then again amines are getting hydrolyzed under
the acidic condition to afford homologated sugar located carbohydrate the d ribose and
its two e primer the
so a pair of c two epimers are getting received where the one carbon is extra
than the d e throws
so this is a total you know protocol is known as kiliani fischer synthesis where we are increasing the you know sugar ah length by one carbon and you know at
the same time we are having you know ah hydroxyl group also now i will since i
discussed about the lengthening of the chain now i am going to talk about the shortening
the chain how how we can shorten the chain how chain saturning can be done and the protocol here is known as whole degradation again i will like to repeat in the lengthening
of chain ah i discussed that you know how starting from a four carbon sugar we
can reach to the five carbon sugar and what are the ah you know transformations
ah required in the kiliani fischer synthesis ah first sugars reaction with the
you know ah hcn are ah cyanide group which which will generate basically cyanide
group
so carbonyl reacts with the cyanide group and the sugar is chiral
so it will generate ah
diastereomer that is the diesel selective reaction and ah this cyanide reaction on the carbonyl
will form the cyanohydrins these cyanohydrins are getting reduced with the deactivated palladium ah
to give partial reduction into the corresponding e min and this amine is getting hydrolyzed to the
aldehyde in the acidic condition to generate the a pair of c2 epimers of the you know base which

which are different at the only second ah carbon ah in the stereochemistry ah basically it is a
d ribose one is d ribose and another is epimer
so we saw that how one carbon can be increased
in ah erythros now we are going to discuss about that you know how ah one carbon can be certain
how certainly can be done and for that ah the protocol is known as hole degradation so
let us talk about the whole degradation now here i am going to take starting material
hexose d glucose basically
so i am writing here d glucose now this d glucose will be reacted with the hydroxyl amine under acidic condition a trace of acid is also
required to facilitate that transformation trace acid is required in
presence of hydroxylamine ld carbonyl will react and it will form auxin exam is formed now this auxilim will be reacted with the acetic anhydride s t can hydride at hundred degree centigrade the s t can hydride will form the acetates whatever the hydraxial group are available in the whole scaffold
it will form the acetate
so and since acetate is a good living group
acetate will eliminate in the form of acetic acid to form nitrile in the exam case
so axam will get converted to nitrile now what we will do that ah we will treat
it this acetate with the base aqueous base aqueous base will do two things it will
hydrolyze all the acetate in the scaffold and under the basic condition again scm
removal will take place from the scaffold and acl removal will generate the aldehyde this is
just reverse of cyanohydrin formation you can see under the basic condition that gives d arabinose which is a pen pentose we saw here that we started with the we started with a d glucose a hexose and we end up in one carbon less a pentose d arabinose again i will repeat the whole shortening process whole degradation which is
known as whole degradation the whole degradation is opposite of the kiliani fischer synthesis where
the certain by one carbon is going to take place in the whole carbon chain here what is happening
that in the first step aldehyde reacts with the hydroxyl amine to form axain this is the axain
in this scaffold it forms oxygen and now this exam is getting treated with the s t can hydride
at hundred degree centigrade what happens that in presence of s t can hydride all the hydroxyl
group will get converted to the acetate here you can see that this is an oac form which
is a good leaving group and that will lead to the nitrile formation what will happen that this bond
will break and this acetate will go out ah in the form of stick acid whereas other acetate will
remain as it is
so that will give you you know ah nitrile acetate by reacting with the s t can

hydride again under the basic aqueous solution all the ester group will get hydrolyzed to convert
the you know hydroxyl group and you know as i mentioned that under the basic condition it will
lead to the formation formation of corresponding aldehyde by the elimination of you know sc on so
what am i saying that
so if we are having here nitrile and then after the base hydrolysis
if we are having the cyanohydrin rest of the things will be
the same what happen under basic condition it will abstract this one and this will go like this and nitrile will leave out so scn is going out and that that is how its you
know creating the aldehyde which is one carbon nest because sn will go out and that will generate
the d arabinose a pentose under basic condition so this much about the you know chain certainly now
i will talk about the you know disaccharide so far we discussed about the monosaccharides
now i will talk about the disaccharides disaccharides as the name itself is spelled di di means you know two
so as
we know that in monosaccharide we have one sugar unit ah whereas ah in the disaccharide we are going to have ah more than one two and these two monosaccharides unit are
going to be attached with the hemi acetyl carbon hemiacetal hydroxyl group and the
other hydroxyl group of the another you know ah monosaccharide units
so we
can define it that if the hemiacetyl group hemi acetyl group of a monosaccharide forms an acetyl by reacting with an alcohol by reacting with an alcohol group of another monosaccharide the glycoside that is formed is a disaccharide the glycoside that is
so two monosaccharide links with each other
at the hemiacetal group of the monosaccharide with the another hydroxyl group of the you
know another monosaccharide and the glycoside that is formed is a disaccharide is a disaccharide
so disaccharides
are compound that consists two monosaccharide that is clear that consists two monosaccharides subunits
hooked with each other by glycosidic linkage two monosaccharides hooked with each other hooked together i can say by a glycosidic glycosidic linkage all right
so let us take real example
that what the disaccharides are actually now i am going to dry structure
of a disaccharide ah here i will take two monosaccharides and hook them with each other by ah glycosidic linkage
so here two monosaccharides are linked with alpha one four prime four prime why i have used one is this carbon that hemiacetal group carbon and four prime is
the other monosaccharide unit the
so here we will say one prime two prime three
prime four prime five prime and six prime
so this is four prime and now this glycosidic linkage

is alpha alpha you can see here that you know orientation up as we have discussed in the case of
enomars
so alpha one four prime glycosidic linkage one four prime glycosidic linkage this is a an acetyl acetyl group again and here if you look over the structure we have hooked together two glucose unit two glucose unit and this disaccharide is known as maltose where two glucose unit are linked by alpha one four prime glycosidic linkage let us take another example where we will have two glucose unit but the glycosidic linkage is
different
so let me draw first now here i had alpha one four prime again in this case also i am having one for one
monosaccharide and four prime for other however the glycosidic linkage is beta one four
prime glycosidic linkage beta 1 4 prime glyco acidic linkage this compound is known as this
disaccharide is known as cellobiose where two glucose unit are attached
so in these both this example in maltose
and in cellobiose what is difference that glycosidic linkage and you can see that monosaccharide is glucose only however both the disaccharides are very different
now i will take the third example lactose where i will use two different monosaccharide lactose
so lactose is different in the
stereochemistry at the fourth carbon and rest are same
so so d glucose d glucose and d lactose d glucose and d galactose are linked together with the again here if we number this is one and here four
prime
so beta one four prime glycosidic linkage beta 1 4 prime glycosidic linkage d glucose and d lactose this both are linked this disaccharide is known as lactose now you saw that ah this disaccharide is also
quite different from the maltose and celebios here glycosidic linkage is same as in the
cellobiose however the constituent monosaccharides are different d lactose and d glucose whereas
they are in cellulose we had two glucose unit
so the nature of disaccharide is completely
dependent on two things the constituent monosaccharide and the type of ah linkages the
glycosidic linkages ah which hook them together in the disaccharide now i will
talk about polysaccharides polysaccharides at the name itself spells out that polysaccharides
contain as few as ten are as many as polysaccharides contain as few as 10 are as many as several thousands monosaccharide thousand monosaccharide units joined together by glycocidic linkages by glycosidic linkages and to exemplify it we will take another ah
polysaccharide starch starch is a polysaccharide starch starch is a mixture of two different polysaccharide mixture of two different polysaccharides what are these two different
polysaccharides one is milos which considered constitutes 20 percent
of the starch and other is amylopectin which constitutes eighty percent of starch let us talk about

their structure that you know how this a myelose and amylopectin looks like ah as
i mentioned in the case of disaccharides ah two monosaccharides are linked together at the hemiacetal ah carbon by the another monosaccharide hydroxyl group similarly here also ah the monosaccharides are linked together at the hemiacetal car
group ah with the another hydroxyl group of the other monosaccharide and that keeps on continue
so ah i would like to make it clear i will like to draw the whole structure over here
so this is a one monosaccharide unit now here you can see that this is
the acetyl ah carbon ah acetyl ah carbon which is linked with the
another monosaccharide hydroxyl group the fourth position of this monosaccharide is linked
so as we discussed in the case of disaccharide
here also since the linkage is alpha and one and this is the four prime so alpha one four prime glycosidic linkage another this keeps on growing
so we can see that this is the linkage
i am coloring it with the red here it is alpha one four prime glycosidic linkage cd linkage here also alpha how do we name it this is one and this is another one is
like you know one prime two prime three prime four prime now again for this linkages this
become one and here it becomes again you know
so that keeps on going three sub units of
here one we have three sub units of a milo's three sub units of milos now i will ah discuss about the amylopectin
that how and
so this way its keep on here i have shown only three subunits but amylose is like you know it is having number of you know monosaccharide linked with the
alpha one four prime glycosidic linkage now i will take amylopectin
so in case of a myopectin what is different i would like to you know explain here
so again here linkages is 1 4 prime
as we saw in the case of mi lows but what is different that not only
alpha one four prime glycosidic linkage but also it has alpha one six prime glycosidic linkage another and
so you can see here that i have
linked it with the another ah unit sub unit with the six
position six prime position glycosidic linkages let me complete the structure
so this has again it is further bonded with the another sub units now let me complete the full structure i
do not want to miss the hydroxyl group i hope now i have completed the all the hydroxyl group now i will mark with red as i have shown here that you know this is these
are the glycosidic linkages in this case it has alpha one four prime glycosidic linkage and here we are having an alpha one six prime you can see here this is one i will use color code here one and
here is that you know one prime two prime three prime four prime five prime and this is six prime
so same way since ah alpha you know explains the orientation of
this linkage
so alpha is the you know ah axial orientation

so alpha one six prime six iterated
with another sub unit six prime glycosidic linkage glycosidic linkage again here we are having one alpha one four prime glycosidic
linkage alpha one four prime glycosidic linkage in total i have drawn here five sub units of amylopectin five subunits of amylopectin which are linked with the
these two type of linkages
so what is different from the m i lows here you
can see that these in amylose we saw that linear you know glycosidic linkages are there but here
we can see that you know two linear ah chains are linked with each other
so strength wise a
myelopectin is more stronger in comparison to the you know a milo's only ah in starch and
basically ah you know starch is a mixture of twenty percent of a milos and eighty percent of
amylopectin now i will talk about the another polysaccharide cellulose cellulose cellulose is the major
structural component of plant and to example fight i will take example of cotton carton we know you know that is the i will say that starting material
for the our clothes you know cotton for example is composed of about 90 percent of cellular composed of about 90 percent cellulose cellulose let me write
this structure that how does it look like as i mentioned that you know in the case of starch
which is a mixture of a milos and amylopectin various sub unit of ah monosaccharides are linked
through the glycosidic linkage in the case of amylose whereas in the case of amylopectin the
various you know subunit are interlinked through the glycosidic linkage also
so linearly they
are linked with the glycosyl linkage and also the two linear chains are linked with each other
also with the glycosidic linkage by using this hemiacetal ah you know carbon ah hemiacetal
group of the first position carbon of the you know ah sugar ah now i will draw the structure of cellulose
so here again as i mentioned that hemiacetal group will
be involved in making the glycosidic linkage what is different over here what is difference over here from the milos that a lot of hydrogen bonding involved
so so first i will like to show you
this ah glycosidic linkage here beta one four prime glycosidic linkage linkage
so one for and this is the
hydrogen bonding involved here i do not want to leave the hydroxyls
so you can see these two hydrogen bonds three subunits of cellulose three sub units of cellulose
so we here we saw that glycosidic linkage is beta
one four prime glycosidic linkage and this is a linear in the case of cellulose however the extra
thing is that hydrogen bonding involved with the you know basically pyramic oxygen a ring oxygen
with the hydroxyl group of another ah subunit
so this much about the polysaccharides ah
now i will like to discuss few problems on this topic basically ah on the carbohydrates

so problem one
so the correct statement i am taking it from the earlier question papers the correct correct statement about the following disaccharides disaccharide is disaccharide is
so let me draw the structure of disaccharide first quickly
so this is the dissect right now i will like the like to write the statements what are the statements first statement is here we are having two ring ring a and ring b this statement is ring a is pyranose with alpha glycosidic link b statement is ring a is furanose with alpha glycosidic link c is ring b is furanose with alpha glycosidic link and final statement is ring b is pyranose with beta glycosidine with beta glycosidic link now you can see here one thing is clear that one is pyranose a is pyranose and b is furanose
so to look over all this four statement a has to be pyranose
so a has to be pyramid whereas but the glycosidic link glycosidic link is here you know alpha because it is a down
so it is alpha so here ring a is pyranose with the alpha glycosidic ring this is the correct statement whereas ring a is furanose this is wrong a is linga is pyranose with alpha glycosid this is the correct part again ring b is furanose that is correct with alpha glycosidic link here ah glycosidic link is not alpha because once you do that that that becomes beta again ring b is pyronose which is wrong with the beta gychositic link this is the correct part
so this way we we eliminated the wrong answer
now i will take another problem problem two cellulose upon a stylation with the excess with the excess acetic and hydride s t can hydride and h2so4 catalytic gives cellulose tie state celu lows tri acetate whose structure is who this structure is
so i will draw the structure all the four structure one thing is clear in the cellulose all the hydroxyl group under the acidic condition will form the you know corresponding acetate and as we know that only three hydroxyl groups are there
so we have to pay attention that you know what kind of linkages are there in the structure and ah what kind of you know ah stereochemistry in this you know cellulose core is there
so that has to be only
so i draw the three sub units here and let me complete the first option of this similarly the please pay attention that linkage in the case of cellulose i told you that beta linkages are required and the structure what i have drawn here it has beta linkage and it has the you know tri acetate

so this is the first second one is having beta glycosidic linkages but the other hydroxyl groups are not in the acetate form they are just you know hydroxyl

so this is eventually not the triacetate it has just

so this is i will not draw the all these all the four isomers because i have already drawn to the other possibility this is the wrong just to here you can see that in the first case we are having acetate triacetate and the linkages here are beta which is the you know kind of cellulose structure beta ah one four prime which is available area and the triacetates are there one two three

so this is the correct where the all the other you know wrong ah options are not i have written here another wrong answer with you know also the last question i will take problem three that following carbohydrate is carbohydrate i am drawing the four options are a keto hexose keto hexose second option is an aldo hec hexose hexose third option is an alpha fura nose and fourth option is an alpha pyranose one thing is clear that it has pyron ring and it has

so pyranose you know you can see that you know alpha it cannot happen because you know it is beta orientation is beta

so we cannot say

so these two are wrong and it cannot be keto hexose ah it can be an aldo hex hose because it will you know from the l d height and high ductile condensation this ring has formed

so the correct option is b ah i will stop here ah

so ah today we discussed about the chain lengthening chain sharpening in the carbohydrates ah we have also discussed about the structure of disaccharides and polysaccharides and we have ah solved some ah related problems

so these are ah six lectures in the carbohydrate ah we have completed and ah in the next lecture i am going to talk about amino acids and proteins thank you very much for you