hello everyone i welcome you all in fifth lecture
of biomolecules before ah going to the main course   of ah fifth lecture i would like to give a
recap of ah lecture four ah in lecture four   we have discussed about ah you know glycoside ah
formations we have also ah discussed about its   mechanism ah we talked about ah reducing
and non reducing sugar we talked about   a numeric effect and we ah we discussed about
the how do we monitor how do we measure the   blood glucose level ah in the diabetic present
that basically what reaction involve over there   these all things we have discussed in
lecture four again ah continuing with the   same ah part carbohydrate carbohydrate
chemistry today i am going to discuss about   the reaction ah reactions of monosaccharides
in basic solution reactions of monosaccharides in basic solution what happens to monosaccharides if
they are ah taken in the basic solution   basically one chemical phenomena
occurs under basic condition they   go for epimerization
so now i am you
know introducing the term epimerization let me define epimerization what is
epimerization in a basic solution a monosaccharide is converted to a mixture of
is converted to a mixture of poly hydroxy poly hydroxy aldehydes and poly
hydroxy ketones poly hydroxy aldehydes and poly hydroxy ketones
how does it happen let us look at you know the   mechanistic parts that you know what happens you
know to d glucose if it is treated with the base   and what kind of chemistry takes place so
i am going to draw structure of d glucose
so this is d glucose d glucose is getting treated with the base as i
told you in the under basic condition
so here i am   taking base in presence of base base will abstract
this proton at the alpha position to the carbonyl and that converts it to to the c2 epimer
so it will abstract proton and it will form h2o and it will get converted to innovate corresponding innovate
so so this is the inolate ion inolate ion now this enolate ion can again go back in presence
of ah water molecule it can go for reprotonation
so this is the c2 position c2 position under basic
condition obstruction of proton is taking place   and it forms the inolate ion again this enolate
ion now this is you know ah sp two hybridized   this ah carbon and it can go back again for
the reprotonation if this lone pair pushes back now two possibilities exist over here one is
the either from the top face protonation can   take place and other this protonation
can take place from the bottom face
so if it is taking place from the bottom
face then it will generate another molecule another aldi hyde and this is
another ah aldo hexoses d mannose d mannose plus hydroxyl group ah will be there

as a
you know side product
so what happens in this base catalyzed epimerization let me
again repeat it this base catalyzed epimerization first thing base removes a proton from the
alpha carbon forming an enolate ion notice that c2 in the enolate ion is no longer
an asymmetric center because this you know it has been converted from sp3 to sp2 hybridized
center
so it is no longer asymmetric center now when this c2 is getting reprotonated
the proton can come from the top face from the top face or it can come
from the bottom face forming both d glucose and d mannose if it is coming from
the top face then it will form d glucose and if it is coming from the bottom
face then it will form d min menus d mannose
this is the c two epmer c two c two epmer this is c two e primer
so we saw that
in presence of base an aldo hexose can epimerize to another aldo hexose basically
the ah second position stereo center gets degenerated and from sp3 hybridized carbon to it
get converted to sp2 hybridized carbon and again after the reprotonation of the inolate ion that
generates the mixture of you know aldo hexoses ah where the other compound is epimeric
at the two position of the same ah what the starting material we had in case of
d glucose under basic condition it can lead to the mixture of d glucose and the c two tumor d
mannose through the you know discussed mechanism now i will discuss about the this ah epimerization
in detail the particularly this rearrangement process that how how is it happening basically if
you see we had one fixed stereochemistry at the c2 position and we degenerated that
c2 position to the sp2 hybridized center and then again by the reprotonation
we have generated a mixture since these all transformations are in equilibrium so
let us discuss in diol rearrangement in dial rearrangement what happens that
during this process what the epimerization i just discussed in addition to forming
its c2 primer in a basic solution d glucose also undergoes an in dial rearrangement which forms d fructose
so in addition to farming it is a c2 epimer in a basic solution d glucose also
undergoes also undergoes an in dial rearrangement an in diary arrangement which
forms d fructose which forms d fructose how does it form d fructose
d glucose how does it form d fructose and subsequent again this d
fructose can further go for the you know subsequent in dial rearrangement to form the other
keto hexoses because d fructose is keto hexose again it can go under the basic condition
for the subsequent in dialy arrangement to form the other keto hexoses and

that way
the carbonyl group will keep on traveling   across the chain
 so let me explain that in dial
rearrangement i will start with the d glucose d glucose reacts with the base as we saw as
we saw in the case of epimerization to form inolate iron inolate iron now this inolate iron can go for again protonation
with the water molecule and that will give corresponding in dial
 so this is in dial forms as an intermediate in dial now this in dial   can again what the hydroxyl group is there in
the reaction mixture can go for the deprotonation and it will generate the enolate ion again inulate iron now this inolate ion can go for the protonation again this negative charge will pose
and it will go further protonation plus
 so again that protonation
will take place from water molecule
 so water molecule is there which will
generate hydroxyl it will give d fructose let me explain it again this whole reaction
process base removes a proton from an alpha carbon   forming an enolate ion now this enolate either c
two can be if we push this lone pair then it can   go for the further protonation at the c2 position
to generate the d glucose and its epimer are if it   gets protonated it forms in dial now this in dial
has two hydroxyl group it has two hydroxyl group   now if deprotonation of the first hydroxyl
group is taking place then again its end up   in going to the d glucose are you know d mannose
if deprotonation of the second hydroxyl group of   the in dial is taking place it will generate d
fructose after the you know ah tautomerization   another in dial rearrangement basically again
push ah the carbonyl group one carbon down   as we saw that you know we started with
the aldo hexoses and we end up with the   you know ah keto hexoses and again if we do in dialysm with this d fructose   with the same sequence of reaction again
you know carbonyl group can move ah further   one carbon down to understand in a better way this
re in dial rearrangement i will take one problem
 so lets solve a problem when d tag a twos is added to a basic equal solution aqueous solution and equilibrium mixture of of monosaccharides is obtained equilibrium mixer monosaccharide is
obtained two of which are aldo hexoses aldo hexoses and two of which are keto exosis identify the eldo hexages
and ke2 axis now identify aldo hexoses and keto exosis
 so our job is to identify the
aldo hexoses and keto excesses   what forms from the d tagger twos now
i will write the structure of d tagatos
 so let us take d tagatos keto hexose basically d tegatos if you remember classification of monosaccharides
i have discussed this structure over there all right
 so i will number it here to make it

more ah current two three four five six now under basic condition what will happen that again alpha to the
carbonyl proton abstraction will take place   and that will get converted to in dial
in dial
 so i am writing here in dial   now it has two alpha position one null proposition is carbon number one and other   position is carbon number three
 so here i
am abstracting carbon number three proton and converting into end ir now this asymmetric center has been degenerated now again if in dial rearrangement is taking
place under basic condition   two possibility exist over here if abstraction of   this proton is taking place then it will get
converted to exosis with the mixture mixture of   that where the protonation can takes place from
the top face or protonation can take place from   the bottom face
 so two stereoisomer will get
generate let me write those two stereoisomer one this one and in other where hydroxyl group is right hand side
 so this is d tagatos we we got the same
starting material after the epimerization same is starting but we regard
the mixture with same starting   material daggertoes and d sorbos
 so this is d tag toes and this is d servos this happens if react if
deprotonation is taking   place at the third position if
deprotonation takes place at the first position if attack so
i will attack at the c one attack at c one here attack at c three base attack at c three
 so attack at c one
 so base bill abstract this proton and it will form inolate now in late is firm
now this enolate can again go for the protonation this can go for protonation to
form in dial again in dial is firm and this in dial will again go for the
deprotonation and this deprotonation of the hydroxyl
o h leads to the eldose formation   followed by protonation at the c two
position now again protonation can happen   from both the faces from the top face
or from the bottom face if it happens   from both phase you know that will lead to the two
corresponding stereoisomers of the aldo hexoses
 so this is d talos d talos and in the other case
 so if from the bottom face then d tallows and
if from the top face then it will form d lactose
 so another deglack toes
 so we started with the d tagatos and we end up in the with the
mixture of d tagatos d serbos d tallows   and d galactose d lactose
 so basically we got the
two eldoses and eldo hexoses and two ketohexoses   through this reaction and in totality what
is happening basically it is a in dial for   rearrangement through the scaffold is taking
place where again you know deprotonation and   reprotonation is happening through this process
and what did we observe ah that in the d tiger   toes where carbonyl as that is at the two position
it it is getting transferred either upside or it   it can get transfer at the

downside if it gets
downside then it can travel again across the chain and if it travels upside then it can get converted
ketos can get get converted to a dose
so that is very good example to understand
so if you treat
the tree tagatos to a basic aqueous solution you know equilibrium of a monosaccharide will
have various eldos aldo hexoses and keto hexoses now let us talk about the you know reactions of these you know monosaccharides particularly
oxidation reductions of monosaccharide oxidation reduction reactions of monosaccharide oxidation reduction reactions of monosaccharides since monosaccharides contain alcohol functional
groups and aldehyde are the chemistry delivered by monosaccharide should be the you know
ah transformations of corresponding groups transformation of hydroxyl group transformation of
ketone group transformation of aldehyde group and the reactions of ah you know monosaccharide you know can be a classified in a way that you
know the this this can react if if it is aldose ah then it should react with the nucleophile if
it is ketose then it should react with the ah nucleophile ah and if it is hydroxyl then again it
can you know give the ah required transformation ah whatever the alcohol groups ah gives so
let us take first you know reduction reaction
so here i am taking d mannose which is aldo hexoses and i am treating it with the reducing agent
reducing event is here sodium borohydride d mannose reduction by sodium borohydride
will convert aldehyde into alcohol and it will form primary alcohol aldehyde will get converted to primary alcohol it will generate after the reduction d manitol manos will generate d manitol d manitol and l d tall since it has been derived
from you know aldehyde it is also known as an l d tall if you start with the d fructose again sodium borohida here also you
know protonating agent is needed and i have hydronium that you know acid reagent is needed again if
you do sodium borohydride reduction and the second hydronium species now since this this carbonyl can get attacked
from the toughest by the hydride ion or it can get attacked from the bottom face
if it get attacked from the bottom face then it will give glucital but if it gets attached
from the top face then it will give manitol it will generate two stereo isomers
so if it is
getting attacked from the you know bottom face then it will generate d manitol but if it gets attached from the top phase
so again sodium borohydride and second is hydronium species that will give reduced compound where hydroxyl is at the right side
so this will give d glucitol deglucital now what is
difference between d manitol and only the orientation of hydroxyl group
in one case it is left in the case of demonital it is left hand side and in the

other case it is right hand side if you see
so by the ketohexoses reduction we are
getting mixture of the two alcohol d manitol   and d glucetol this is also you know an
ldtol d glucital also called serbitol d glucitol also called servitol is about 60 percent as sweet 60 percent as sweet as sucrose it is found in plums peers cherries and berries cherries and berries it's a 60 percent as
sweet as sucrose now let us talk about the   oxidation reaction
so we discussed you know
reduction in the reduction we saw that you know   mannose can get reduced to the manitol whereas
if we start with the keto hexose d fructose d fructose d fructose it will give a mixture of the product if the hydride will attack
from the top face then it will give deglusital   if it attack from the bottom face then it will
give d manitol these two product ah are possible now let us talk about the oxidation d glucose after the oxidation generates
d gluconic acid what is the structure of   d glucanic acid that can be easily generated from the d glucose d glucose in presence of bromine water gets converted to aldehyde group
gets oxidized to the carboxylic group and it gives d gluconic as well as it generates
bromide iron in the reaction mixture which is   colourless
so how how can we figure out that you
know rex oxidation reaction has been completed   if we take d glucose and treat it with the bromine
water ah it will bromine water which is you know   basically red is brown in color because of the
color of bromine and after the reaction basically   aldehyde group will get converted to
acid it will form the d gluconic acid t gluconic acid and it will generate bromide
iron
so the reddish brown reddish brown color of brown color of bromine after the oxidation of
monosaccharide glucose to the gluconic acid bill   because of it gets it gets converted to the
bromide will disappear it will become colorless basically bromide is getting reduced say
bromine is getting reduced to bromide   and glucose is getting oxidized to gluconic acid both aldos and ketosis are
oxidized to aldonic acid
so if you take both eldoses and ketosis are oxidized oxidized to aldonic acid by tolerance region by tolerance reagent what is tolerance in a monocle you know silver
nitrate a g plus n h three and o h i mentioned   silver nitrate is what we say basically the
mixture contents
so first we discussed about the   oxidation of you know glucose with the bromine
water where it gets converted to gluconic acid   where only aldo hexoses has been converted
however if we want to convert both l doses and   ketosis if we treat with the tolerance reagent

they get oxidized to the you know aldonic acid
so let me write the structure i am writing here representative
structure for the ketosis ketos   under basic since the tolerance reagent is
having a monocle you know cellular nitrates   basically you know it has base
also and a
g plus is there
so under basic condition   as we discussed that you know it can
go for in dial ah rearrangement and   because of the end dial rearrangement
it will get ketos can get converted to   aldos basically ketos can get converted
to eldos
so it will form a aldose now this aldose
in presence of a g plus and ammonia can get converted to carboxylate ion by the
oxidation of l d high to carboxylic group that is why you know tolerance
reagent can oxidize eldose and ketosis plus silver is zero firms the oxidizing
agent in tolerance reagents tolerance reagent is a z plus it
is reduced to the metallic silver   it is getting reduced to
the metallic silver ag zero   that forms on the inside of the test tube when we
do reaction basically when we treat eldose and ah   ketos with the ammonical
silver nitrate which
is basically basic in nature
so what happened   that eldose gets converted to corresponding ildos
and then a z plus oxidizes it to the you know ah   carboxylic group aldehyde
gets converted to
the carboxylic group and that thats what that   is the reason ah it it can
oxidize both eldos and
ketos because under basic condition all the ketos   gets converted to the l dose
so ah the oxidizing
agency tolerance reagent is in tolerance reagent is silver plus it is reduced to
which
gets reduced to a z metallic silver   basically forms metallic silver it gets
deposited on the on the test tube wall   although tolerance reagent only
oxidized
aldehyde it can be used to distinguish aldos   and ketos the oxidation reaction
is carried out in
a basic solution that will convert a ketose to an   eldose by an in dia
arrangement and the aldos
will then be oxidized by tolerance reagent
so again i am repeating ah although tolerance
reagent only oxidized aldehyde it cannot be used   as a distinguishing reagent
between the eldoes
and ketos because it it requires basic ah reaction   condition and basically
reaction condition will
convert ketosis to aldoses and then again aldos   will get oxidized to the ah
corresponding
you know ah aldonic acid ah now i will   introduce another final oxidizing
reaction the
oxidation reaction in presence of nitric acid in presence of nitric acid it
converts even primary alcohol
to the carboxylic acid and the aldehyde group also gets converted
to carboxylic carboxylic group
so it gets converted to dicarboxylic acid d glucaric acid d glucaric acid and
alderich acid dilute nitric acid is a stronger oxidizing addend
and it oxidizes l d hydric group two carboxylic   group as well as the you know
primary alcohol

group to the carboxylic group it does not touch the secondary ah hydroxyl group if you see that you know this poly hydroxy aldehyde is having multiple you know secondary hydroxide but it does not touch only the primary primary alcohol group is getting oxidized to the you know carboxylic group and aldehyde group is getting oxidized to the carboxylic group it forms d glucaric acid so now i will stop here ah to conclude we have discussed about the you know different reactions of you know a monosaccharide in basic condition and there we talk about epimerization we talk about in dial rearrangement ah we also ah talk about you know different ah you know ah in dial ah related ah you know problems that you know how ah a ketos can be converted ah to the mixture of eldos and ketos under ah if it is kept under basic condition ah by taking the detectators problem we have also ah discussed about the you know reduction reaction of monosaccharide and we saw that how aldehyde can be converted to the primary alcohol whereas ah you know ah ketos ah you know in the case of eldos it will get the corresponding you know primary alcohol d mannitol ah if we start with the aldo hexose however if we start with the keto hexose that will give mixture because that you know they are hydro the carbonyl of the you know ketos will get attacked from the bottom face are from the top face and that will give the corresponding you know ah you know i mean alcohol secondary alcohols by the reduction of the ketone group ah we have also talked about the oxidation and oxidation we discussed that you know how um oxidation with the bromine will lead to the ah you know um of the um ah eldoses to the aldonic acid if we take aldo hexoses that will form the aldonic acid ah however if we take ah ketosis i mean treat them with the ah i mean tolerance reagent that are oxidizing the agent ah that will also get ah i mean oxidized to the aldonic acid ah because the tolerance resin has a ah basic ammonium ammonical ah you know silver nitrate and they are the oxidizing agent in silver plus ah however because of the presence of the basic condition the ketos can get converted to the ah you know ill dose and that eldose ah forms the aldonic acid um tollens resin can also oxidize enddoses to the aldonic acid

so tolerance agent can oxidize both eldose and ketosis the one important point here is that we cannot use tolerance reagent as a distinguishing oxidizing

reagent ah between the
eldos and ah ketosis because it oxidizes both ah   ah also the eldosis can be oxidized by the
dilute nitric acid and there we can get   dicarboxylic acid the aldehyde group of the
eldose aldoxes get oxidized to the carbon   carboxylic group and the primary alcohol group
ah gets oxidized to the carboxylic group and that   generates the glucaric acid if we start with the
glucose it forms the d glucaric acid ah however   the secondary hydroxyl group does not get oxidized
ah now i will stop here we will again continue   ah with the carbohydrate chemistry ah
in the next class thank you very much you