hello students i'm Pearl Dos Santos
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women
Nuvem Goa i'm going to look at
bachelor of science second year topic,
chemistry semester 3 chc 103
physical and organic chemistry we are
looking at
nitration of aniline which comes under
the chapter
amines and diazonium salts
this is the outline
we are going to look at ring
substitution in aromatic amines
and nitration of aniline
what the outcome must be is to interpret the
concept of electrophilic substitution
exemplify electrophilic substitution on
aniline
and explain the mechanism involved.
so before we go on let us brush up our
basics
starting with what is an electrophile
an electrophile is an electron deficient
species
and a nucleophile is an electron rich
species
we also know from our lower classes that
substitution
on the aromatic ring can influence or
direct the incoming electrophile
either on the ortho para or meta
positions
in the case of electron donating groups
it is directed towards the
ortho and para positions and in the case
of electron withdrawing group it is the
meta position okay
in other words 3- position is
meta
2 & 6 which is ortho and 4 which is
para in the case of aromatic amines
the functional group is NH2, NH2 is an
electron donating group
it activates the ring and it activates
the ortho and the
para positions.
this is the structure of
aromatic
amines so if you look at this,this is
the ortho position the para position
and the ortho position again so let us
see
why is it that these amines direct the
incoming electrophile
on the ortho and para positions only
we
can explain this by
resonance so in the resonating structure
if you go to see
i have drawn it over here if you look at
this positions over here

with the negative charge which positions
are these
2 4 and 6. Now having the negative
charge
means what
essentially it means that
these are the regions of
high electron
density in other words they are
more nucleophilic
so since these positions on the aromatic
amine are
more nucleophilic the substitution
occurs at
ortho and para positions
now that we've understood this let us
come to the topic which is
nitration of anilines so the nitrating
mixture as we know
is concentrated nitric acid and
concentrated
sulfuric acid mixture let us see what
happens when we treat Aniline with this
nitrating mixture so
if you treat aniline with the mixture
what happens you get your para product
you get ortho product but you also get
the
meta product in fact
the meta product is formed in
major quantity okay
so now having meta product formed in
major
quantity just contradicts all that we
have studied
correct so let us see why this meta
product is
formed
the meta product is formed because of
the formation of this
anilinium ion okay so basically what
happens
is you have aniline
and you have your nitrating mixture
essentially this nitrating mixture is an
acid source so it is a proton donor
and amines are organic
bases so what happens you have an acid
based reaction forming
giving you the formation of this
anilinium ion
now if you look at aniline
Aniline has NH2 which is electron
donating
and that is why it activates the ortho
positions
and the para positions but if you look
at this part NH3
plus is formed this is no longer
electron donating
rather it becomes withdrawing in nature
by the

- I effect
okay so because it becomes withdrawing
in nature
now it activates the meta position
so to avoid the formation of this meta
position
what is formed is the anilide
basically we are protecting
aniline
to give the acid anilide and the
nitration
is made to form on this anilide
so this is how aniline is converted to
Anilide acid anilide
what happens aniline is treated with a
Acetic anhydride in presence of pyridine
to give you the formation of acid
Anilide
once this is done
nitration is made to occur on this acid
Anilide
giving you the formation of para
nitro acid anilide
okay then what is done
you also get some ortho product but this
is in
minor quantity
so moving on this para nitro acid
Anilide
is then hydrolyzed
to give you para nitro aniline
all right
so let us move on to the mechanism what
happens is
there's a generation of your
electrophile first which is your
nitronium ion
this nitronium ion is then substituted
on the
aromatic amine i have showed the
mechanism for the para product because
it's the major product
so how will you show the mechanism you
will first show the
involvement of the lone pairs bring this
down over here
and this bond will attack the nitronium
ion to give you this
formation then we have the
re-aromatization
this H is picked up by the counter anion
HSO_4^-
picks up this proton these electrons
fall here
this comes here and this goes back here
to give you your final product
this then is hydrolyzed like mentioned
earlier
to give you para nitro
aniline okay
these are the references
thank you