

Hello and welcome I'm Dr. Mira

Parmekar from St. Xavier's College Mapusa-Goa.

I'll be taking up module for the third year,

Bachelor of Science, today in the

subject of chemistry for semester six

in the paper CHC 110 that is organic

chemistry and this module comes in

the section A of it under the unit.

Name reactions, and rearrangement and

I will be dealing with two name reactions,

that is, Dieckmann and Stobbe,

Condensation.

Overview:- The presentation will be first,

will introduce what basically

a condensation reaction is,

then go about individual reactions.

Study some important applications

and finally summarize. Dear students,

Do make it a point to come back to

this slide and make sure that after

you see the recording of this video,

you can fulfil all the outcome

of this particular module.

So condensation reaction since

both the reactions are condensation,

Let's try to understand what

a condensation reaction is.

It is a class of organic addition

reaction that typically produces

an addition product with loss of

a small molecule such as water,

ammonia, ethanol and so on.

So basically what reaction you can

see at the bottom of the screen.

OK, I have an alkane,

RH which is reacting with our RX, X can

be anything it could be OH, NH₂ Cl₂ etc.

What is happening is I'm getting in

addition product so R-R is forming as an adduct.

OK I am getting a big molecule.

from smaller Fragments and in the

process I'm losing a small molecule,

HX. Now if you substitute the X

here, leaving molecule could be either

water or ammonia, alcohol, etc.

OK,

so that becomes the sacrificial

part or sacrificial molecule for

the formation of your adduct.

Coming to the first name reaction

recommend condensation.

Diekmann condensation is the

intramolecular chemical reaction

of diesters in presence of a base,

and it gives you beta keto esters.

This reactions is given by diesters

1,6 or 1,7- diesters

in presence of base.

What will happen is it will

give you a cyclic product.

so you need to understand and apply

to the ring to get the final product.

That is the reason it is written.

I said in the second step and sacrificial molecule in this particular name reaction is a small molecule of alcohol. You react and the resultant product is either a 5-membered beta keto ester, if you start from 1,6 or if you start from 1,7 diester, it will be a six membered product.

So what are the highlighting features of this reaction?

It is a name reaction named after a German chemist, Walter Dieckman.

It gives you either five or six membered cyclic beta keto Ester from a diester and it is actually equivalent to a Claisen condensation reaction.

Claisen condensation reaction,

There will be a separate module.

You can see that video as well to understand it.

So what is the general reaction

for this particular reaction?

Is you have a 1,6 diester,

how do we name it 1,6 OK?

This is my ester group.

This is my second Ester group.

OK, I'll go from your 1,2,3,4,5,

OK, 6 Carbon Ester so

it becomes a diester 1,6 diester.

though if I'm creating a diester.

OK what I'll be losing in the process

is a ROH molecule that is alcohol OK

and there will be our bond formation.

So if you know this will

be 1,2,3,4, 5-membered ring.

OK that is you get a 5 membered

cyclic beta keto Ester.

How it is named OK,

this is your edge carbonyl group.

OK with respect to this, this

is my alpha carbon.

This is a beta carbon beta

carbon is having a carbonyl.

It is ketonic so it is beta keto Ester.

OK, this ticket application,

an important application of Dieckman

reaction is it is used to build up

five or six membered ring in the

synthesis of various natural product,

nature, product,

whatever is synthesized in nature.

When you go to extract they are

available in very small quantities.

So if suppose you want to use

it in industry or medicinal use,

you need to synthesize variants.

This name reaction comes in very very handy.

OK, what kind of base do we use?

We use any.

Alkoxide base OK.

It could be maybe that are made

be methyl alcohol so it will be

maybe methoxide or ethoxide.

or propoxide.

Any alkoxide can be used as the base

along with the corresponding alcohol.

OK what you will be losing here

is 1 Arrow Edge molecule since

this is now 1,2,3,4,5,6,7.

OK this is a 1,7-diester so you'll be

getting a 6-membered ring out of it.

OK similarly if you start with

1,6- we will get a

Five membered beta keto

Ester so this molecules become

very very important when you do

natural product synthesis.

Important application of this reaction

Is, it can be also used to prepare

heterocyclic beta keto esters OK.

The only difference here is previous

case we have taken an aliphatic

diester wherein it was all carbon.

Your one of the carbon has been

replaced by a tertiary nitrogen group.

OK you have two Ester group again.

We will be having a quick

closing of ring here.

OK sorry, closing of ring here.

And you will be getting a 6

member N-heterocycle in this case.

Similarly in second case we're

having sulfur in the aliphatic chain.

So when the reaction undergoes condensation,

you'll be getting again.

This is 1 OK, this is 1,6-,

so you get a 5 membered ring with

sulfur as the heterocycle in the ring.

OK, if you see carefully,

what is the base used?

It is a sodium ethoxide in ethanol.

Corresponding to solvent

Why we require it is because

The product will be in salt form.

You need to acidify and get the solid out.

OK.

Going to the second name reaction

that we have is Stobbe

condensation reaction.

The formation of alkaline succinic

acid or their monoesters by the base

mediated condensation of ketones.

and aldehydes

OK, with dialkyl succinate is known

as the Stobbe condensation reaction.

So if you have an aldehyde or a ketone.

OK, you can do the reaction.

The only difference between this

and the previous, here we are not

changing the diester. The dialkyl

succinate is the only diester which

is used, and what you can change it,

You can take any aldehyde or ketone.

You take this in presence of a strong base.

OK you will be getting a Alkylidene

succinic acid also called as a half

Ester and here the sacrificial molecule

is the small molecule of water.

What are the highlights of this?

OK, this was first demonstrated by

Hans Stobbe in the year 1897.

One important factor which differentiate

it from the previous one is that

this uses a very very strong base.

OK either potassium or sodium salt

Of a hindered alkoxide OK like

tertiary butyl alkoxide.

So this is a very very strong base

as compared to in the previous.

Also one more important factor is it

gives you'll a lactone intermediate

when the reaction happens.

Lactones are basically cyclic esters OK,

and what you get is a half-ester.

I'll explain what is 1/2-Ester.

This is the general reaction of the

Stobbe condensation.

So you start with aldehyde or ketone.

OK as I mentioned previously,

the Ester is constant.

OK, you have to take a succinic diester.

-R could be anything,

Any alkyl group. You take a succinic

diester and what you're losing in

the process is this molecule OK,

two hydrogen, one oxygen makes.

HOH, water- the molecule which is loss

and you get formation of double

bond between these two.

So you get sort of the half-ester

in the first step.

That is the reason you need to

acidify this OK and you will get

the alkylidene. Why this is called

as half Ester basically the reason

alkylidene from succinic diester

is also called half-ester is because

we start with a diester yes or no.

There are two Ester groups OK

but the one is hydrolysed.

In the process it becomes COOH.

So that is the reason.

OK, only one Ester group is remaining.

It is called as a half Ester.

Again one important application of this

is you can get extended chain acids.

So say suppose now this is my acid

of known molecule that I'm starting

where your acid of a known OK

again your diester will remain

same, diester of Succinic acid.

You take a very strong base that is

Hindered or tertiary butoxide of

butanol OK then you acidify it.

You will get your half ester OK once

you get your half Ester OK this is not final.

This is a salt so.

It is a half ester salt, OK,

you treat it with mild acidic conditions.

Maybe acetic, acid,

Or HBr and then when you acidify.

What will happen is since

this is conjugated here,

OK, only this will hydrolyse.

It will become COOH,

and when you're heating, this

will be lost as carbon dioxide.

OK, you can see it is gone from here.

OK, So what you get is you start

with two carbon chain here on your

ring you end up getting a 5

carbon chain on your product.

OK with ending

in an carboxylic acid.

That is what is meant by extended

chain acid from a small molecule.

You're making a bigger extended acid.

OK, second important application of

Stobbe condensation is, it can also

be used to make polycyclic rings.

Again, we start with Acetophenone.

OK, the first process is the same,

you get your half Ester.

OK, it is the same what we

saw in the previous slide.

Only orientation the way it

is written is different,

so you have your half Ester.

Here we're treating it with a

mixture of very strong acid,

sulfuric acid and hydrofluoric acid.

What happens in the process

is there is cyclization.

So you start with the one ring

you end up getting two rings

that is Polycyclic system.

This is basically our Napthalene,

naphthalene derivative.

So that is how basically you do

natural product synthesis of molecule

which are important in medicines.

Or industrial applications.

To summarize,

what we saw is we saw Dieckman condensation,

which gives you a five or six membered

cyclic beta keto Ester from the diester,

and it can be also said equivalent to

intramolecular Claisen condensation

by intramolecular Claisen, we mean

Condensation is between two

different esters intramolecularly,

meaning it is happening within the

molecule between two Ester groups.

OK, this is the general reaction of the same.

Similarly, we also saw Stobbe condensation,

which the difference being,

It uses a very very strong base,

like sodium or potassium.

Sort of tertiary butyl,

alkoxide OK and it gives you a

formation of intermediate lactone.

This is the general reaction

of the same reaction.

You get a half Ester.

The references now,

since it's beyond the scope of the syllabus,

the mechanism is not dealt with.

But if you are interested you can

go to the links given here of the videos.

You'll be able to understand

and relate to the mechanism how

the reaction proceeds.

otherwise Norman and Coxon is

the best book to refer.

Thank you so much for your viewing.