Reagents in Organic Synthesis
Professor Subhas Chandra Pan
Department of Chemistry
Indian Institute of Technology, Guwahati
Lecture 1
Chromium based reagents for oxidation

Key words: Jones Oxidation, PCC, PDC, PFC, Collin's reagent

Welcome again to the MOOC program of NPTEL. Today, I will teach oxidation number and chromium based oxidising reagents. Let us first discuss what is oxidation.

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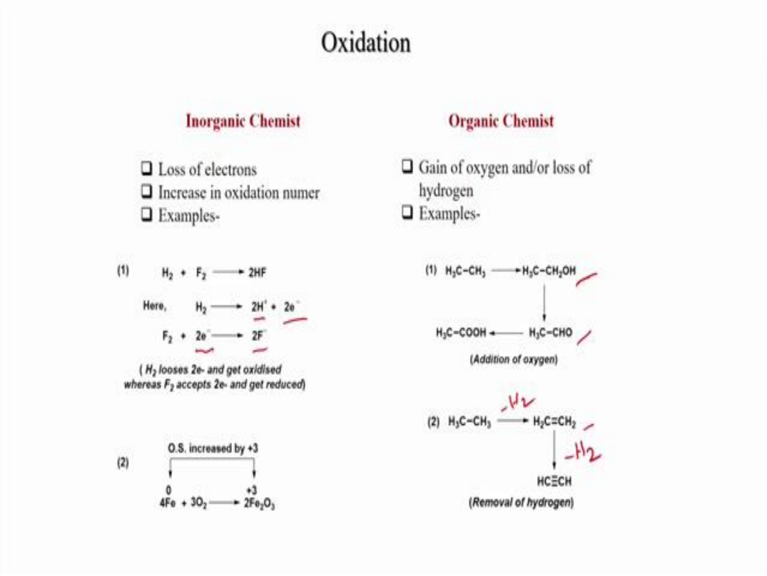

Oxidation

Inorganic Chemist

- ❑ Loss of electrons
- ❑ Increase in oxidation numer
- ❑ Examples-

(1) $H_2 + F_2 \longrightarrow 2HF$

Here, $H_2 \longrightarrow 2H^+ + 2e^-$

$F_2 + 2e^- \longrightarrow 2F^-$

(H_2 looses 2e- and get oxidised whereas F_2 accepts 2e- and get reduced)

(2) O.S. increased by +3

$\overset{0}{4Fe} + 3O_2 \longrightarrow \overset{+3}{2Fe_2O_3}$

Organic Chemist

- ❑ Gain of oxygen and/or loss of hydrogen
- ❑ Examples-

(1) $H_3C{-}CH_3 \longrightarrow H_3C{-}CH_2OH \longrightarrow H_3C{-}CHO \longrightarrow H_3C{-}COOH$

(Addition of oxygen)

(2) $H_3C{-}CH_3 \xrightarrow{-H_2} H_2C{=}CH_2 \xrightarrow{-H_2} HC{\equiv}CH$

(Removal of hydrogen)

For an inorganic chemist, oxidation means loss of electrons, an increase in oxidation number. For example, in the reaction of H_2 plus F_2 when 2HF is forming, if you think about the half reactions; so H_2 is converting to 2H plus and releasing 2 electrons, so it is getting oxidised. Whereas, fluorine, is accepting 2 electrons and it is becoming 2F minus. So, it is getting reduced. Similarly, for reaction of iron and oxygen, if you think the stoichiometry, 4Fe plus $3O_2$, it becoming $2Fe_2O_3$. Here, in free iron, it has oxidation state 0. Whereas in iron plus, here plus 3. So, the oxidation state is increase by plus 3 so, this is oxidation.

However, for an organic chemist the oxidation number is not truly understood that is why gain of oxygen and/or loss of hydrogen is considered oxidation, whereas reverse is considered hydrogenation. Let us see some examples like, when ethane is converting to ethanol, 1 oxygen is adding. Now ethanol is converting to acetaldehyde, 1 hydrogen is liberated. Similarly, when acetaldehyde is converting to acetic acid, it is also taking oxygen. So this addition of oxygen is called oxidation. Similarly, ethane is converted to ethylene where one hydrogen is liberated. Similarly, ethylene converted to acetylene, 1 hydrogen is liberated. So liberation of hydrogen is happening here and this is also considered oxidation.

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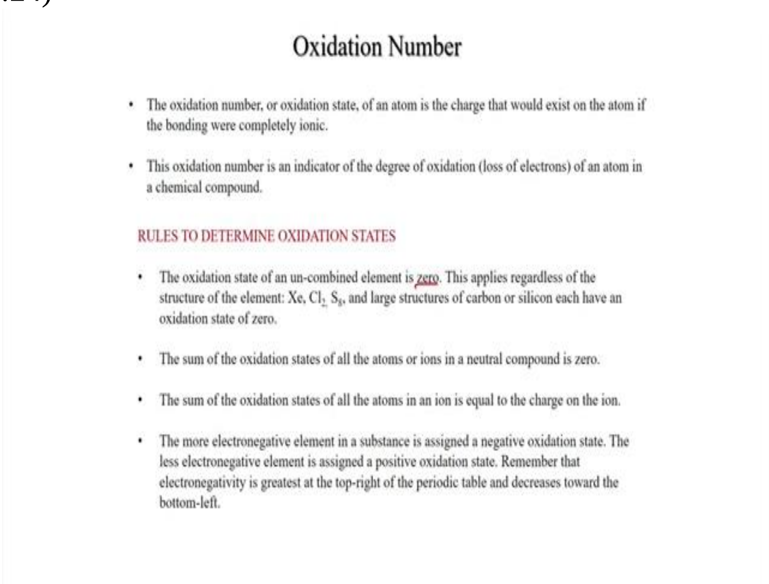

Oxidation Number

- The oxidation number, or oxidation state, of an atom is the charge that would exist on the atom if the bonding were completely ionic.
- This oxidation number is an indicator of the degree of oxidation (loss of electrons) of an atom in a chemical compound.

RULES TO DETERMINE OXIDATION STATES

- The oxidation state of an un-combined element is zero. This applies regardless of the structure of the element: Xe, Cl_2, S_8, and large structures of carbon or silicon each have an oxidation state of zero.
- The sum of the oxidation states of all the atoms or ions in a neutral compound is zero.
- The sum of the oxidation states of all the atoms in an ion is equal to the charge on the ion.
- The more electronegative element in a substance is assigned a negative oxidation state. The less electronegative element is assigned a positive oxidation state. Remember that electronegativity is greatest at the top-right of the periodic table and decreases toward the bottom-left.

So, what is oxidation number? The oxidation number, or oxidation state, of an atom is the charge that would exist on the atom if the bonding were completely ionic. And the oxidation number is an indicator of the degree of oxidation or loss of electrons of an atom in a chemical compound and there are certain rules to determine the oxidation numbers. The first rule is that the oxidation state of an un-combined element is zero, like we have seen in iron last case. This applies regardless of the structure of the element like xenon, chlorine, S_8 and large structures of carbon or silicon each have an oxidation state of zero.

Also the sum of the oxidation states of all the atoms or ions in a neutral compound is zero; this is very important. When we calculate the oxidation state of a particular atom we have to consider that the whole molecule, if a neutral compound should be zero. The sum of the oxidation states of all the atoms in an ion is equal to the charge of the ion. This is equal also for the when we calculate the whole charge of the ion we have to consider this. The more electronegative element in a substance is assigned a negative oxidation state. The less electronegative element is assigned a positive oxidation sate. Remember that electronegativity is greatest at the top-right of the periodic table as you know fluorine, chlorine, and decreases towards the bottom-left.

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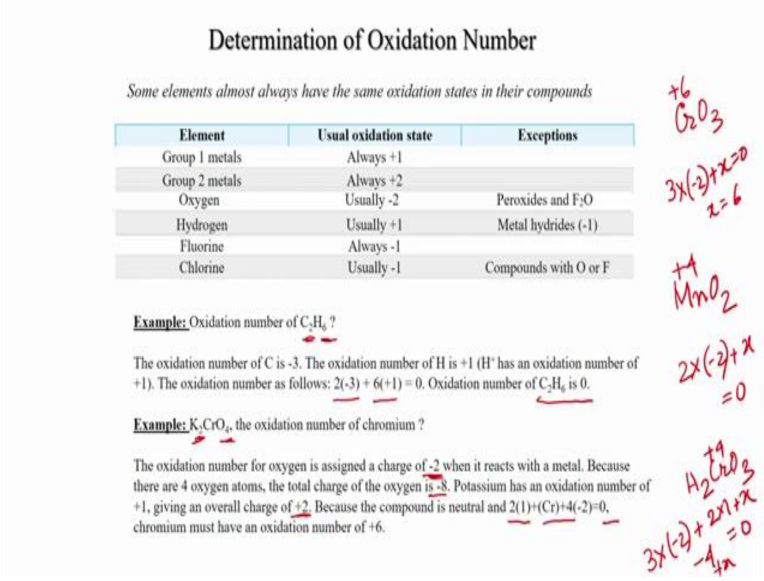

Determination of Oxidation Number

Some elements almost always have the same oxidation states in their compounds

Element	Usual oxidation state	Exceptions
Group 1 metals	Always +1	
Group 2 metals	Always +2	
Oxygen	Usually -2	Peroxides and F_2O
Hydrogen	Usually +1	Metal hydrides (-1)
Fluorine	Always -1	
Chlorine	Usually -1	Compounds with O or F

Example: Oxidation number of C_2H_6 ?

The oxidation number of C is -3. The oxidation number of H is +1 (H^+ has an oxidation number of +1). The oxidation number as follows: 2(-3) + 6(+1) = 0. Oxidation number of C_2H_6 is 0.

Example: K_2CrO_4, the oxidation number of chromium ?

The oxidation number for oxygen is assigned a charge of -2 when it reacts with a metal. Because there are 4 oxygen atoms, the total charge of the oxygen is -8. Potassium has an oxidation number of +1, giving an overall charge of +2. Because the compound is neutral and 2(1)+(Cr)+4(-2)=0, chromium must have an oxidation number of +6.

$\overset{+6}{Cr_2O_3}$

$3\times(-2)+x=0$

$x=6$

$\overset{+4}{MnO_2}$

$2\times(-2)+x$

$=0$

$H_2\overset{+4}{CrO_3}$

$3\times(-2)+2\times1+x$

$=0$

-4, $+x$

Let us see more about oxidation number. Some elements almost always have the same oxidation state in their compounds. Like group 1 metals like sodium, potassium, they have always plus 1 oxidation state. Similarly group 2 metals, magnesium, calcium, they have always plus 2 oxidation state. Oxygen usually has minus 2 oxidation state. However, there are exceptions like peroxides and F_2O. Similarly hydrogen has usual oxidation state- plus 1. However exception is metal hydride where it is minus 1. Fluorine always has minus 1 oxidation state; chlorine usually minus 1. However exceptions are there when compounds with oxygen or fluorine.

Let us calculate the oxidation number of C_2H_6.The oxidation number of carbon here is minus 3 and the oxidation number of hydrogen is plus 1. H plus has an oxidation number of plus 1. Now the oxidation number of the compound as follows. We have to multiply carbon oxidation number with 2 because there are 2 carbon atoms and we have to multiply hydrogen oxidation number with 6 because there are 6 hydrogen atoms. So total oxidation number of the molecule will be 2 into minus 3 plus 6 into 1 that that will become a zero so, oxidation number of C_2H_6 is 0 and this also implies that neutral compound oxidation state will be 0.

Now potassium chromate, what will be the oxidation number of chromium? Here, as I told earlier, the oxidation number of oxygen is assigned minus 2, when it reacts with a metal and now because there are 4 oxygen atoms where the total charge of oxygen will be 4 into minus 2 that will be minus 8. And potassium has an oxidation number of plus 1, giving an overall charge of plus 2 because there are 2 potassium atoms. Now because the compound is neutral and 2 into 1 plus chromium plus 4 into minus 2 will be 0, and this implies that chromium here has plus 6 oxidation state.

Let us discuss some more examples like manganese oxide. Manganese oxide, if you see there are 2 oxygen atoms, so 2 into minus 2 plus ‘x’ is equal to 0. So ‘x’ will be plus 4. Similarly CrO_3, CrO_3, what will be the oxidation number of chromium? Here 3 oxygen atom is there. So 3 into minus 2 plus ’x’ is equal to 0. So x is equal to 6. So here it has plus 6 oxidation state and MnO_2 has plus 4 oxidation state. Let’s discuss this one H_2CrO_3, what will be the oxidation number of chromium. Here 3 oxygen atom is there, so it will be 3 into minus 2 plus 2 hydrogen atom is there, plus 2 into 1 plus X is equal to 0. So, 3 minus 2 is minus 6, plus 2, it is coming minus 4 plus x is equal to 0. So, chromium will be here plus 4. So, this is chromous acid.

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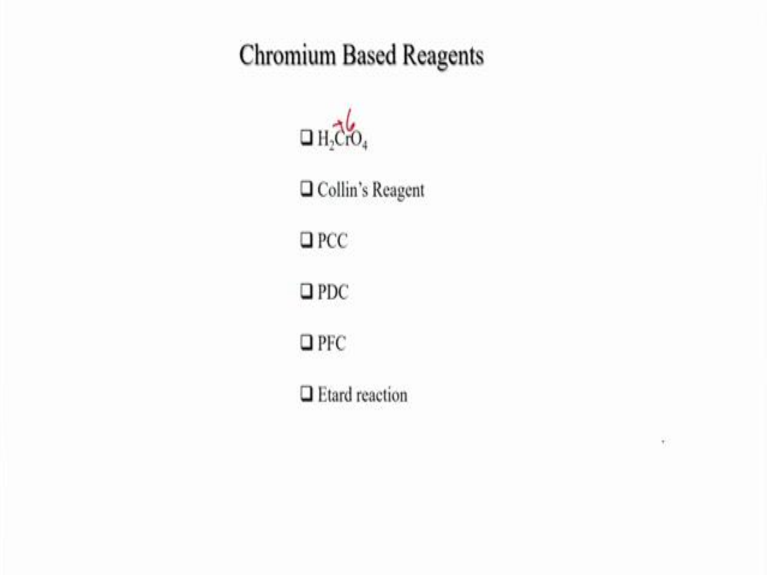

Chromium Based Reagents

- ☐ $H_2\overset{+6}{Cr}O_4$
- ☐ Collin’s Reagent
- ☐ PCC
- ☐ PDC
- ☐ PFC
- ☐ Etard reaction

So, next we will discuss some chromium based oxidising reagents and there are different chromium based oxidation reagents and their reactivity are also different. So, we will discuss one by one. First is chromic acid which is strong oxidising agent and here chromium has plus 6. Collin's reagent which is pyridinium and chromium trioxide we will discuss in detail. PCC which is pyridinium chlorochromate which is mild oxidising agent, PDC this is pyridinium dichromate which is mild oxidising agent, PFC pyridinium flourochromate which is also a mild oxidising agent and Etard reaction, this also chromous chloride we will discuss later.

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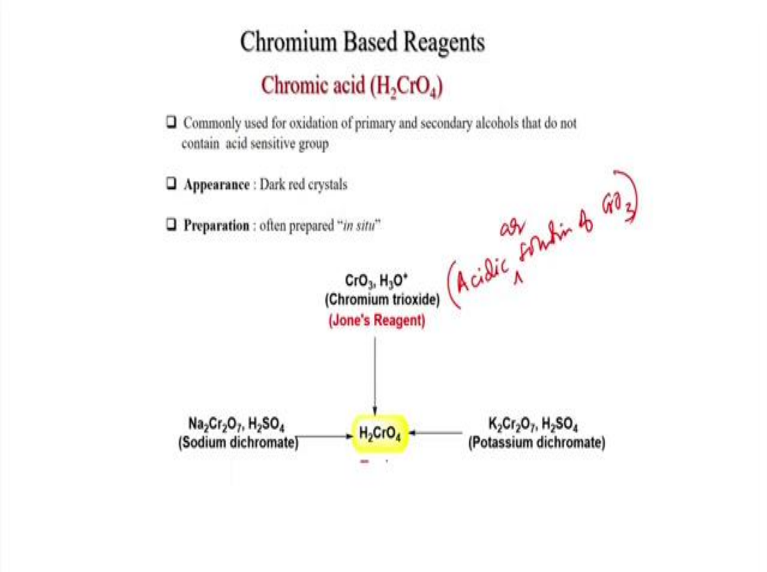

Chromium Based Reagents

Chromic acid (H_2CrO_4)

- ☐ Commonly used for oxidation of primary and secondary alcohols that do not contain acid sensitive group
- ☐ **Appearance** : Dark red crystals
- ☐ **Preparation** : often prepared "*in situ*"

CrO_3, H_3O^+
(Chromium trioxide)
(Jone's Reagent)

(Acidic aq solution of CrO_3)

$Na_2Cr_2O_7$, H_2SO_4
(Sodium dichromate)

H_2CrO_4

$K_2Cr_2O_7$, H_2SO_4
(Potassium dichromate)

So, what is chromic acid? We will discuss more detail now. Chromic acid is strong oxidising agent and commonly used for oxidation of primary and secondary alcohols that do not contain acid sensitive group because it is already acid so, it can hamper the acid sensitive group. It is generally appeared as dark red crystals and mostly it is prepared in-situ. So there are different reagents which can generate chromic acid in-situ like chromium trioxide and H_3PO_4. This is acidic aqueous solution of chromium trioxide. So this is called Jones Reagent and this in fact in-situ generate chromic acid. Also, different salts you can use like potassium dichromate and H_2SO_4 which will generate chromic acid. Also sodium dichromate, H_2SO_4 it can generate chromic acid in-situ.

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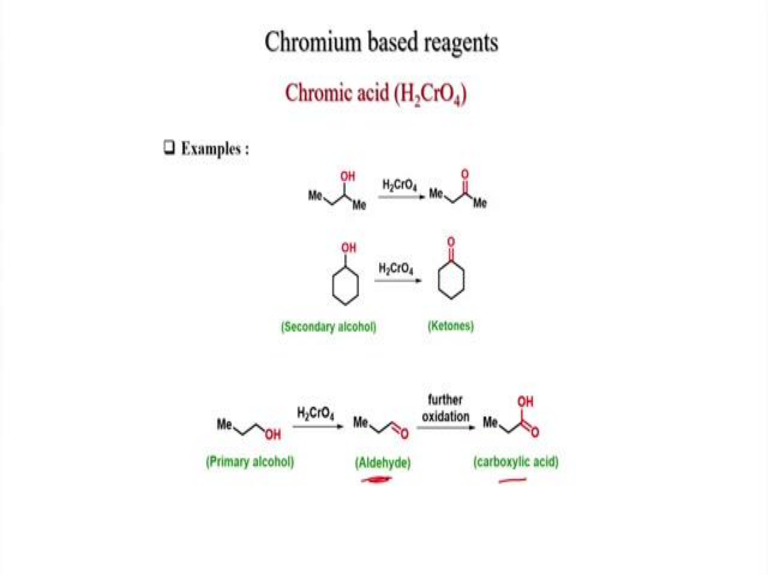

Chromium based reagents

Chromic acid (H_2CrO_4)

❑ **Examples :**

Let us see some examples of chromic acid oxidation. Simple secondary alcohol like this alcohol under chromic acid condition will generate this acyclic ketone. Similarly cyclic alcohol like cyclohexanol under chromic acid condition will give cyclohexanone. And for primary alcohol this oxidation cannot be controlled. So first, oxidation will take place with chromic acid to generate the aldehyde and the aldehyde will be further oxidised to the carboxylic acid. So, that’s why you cannot control the oxidation up to aldehyde.

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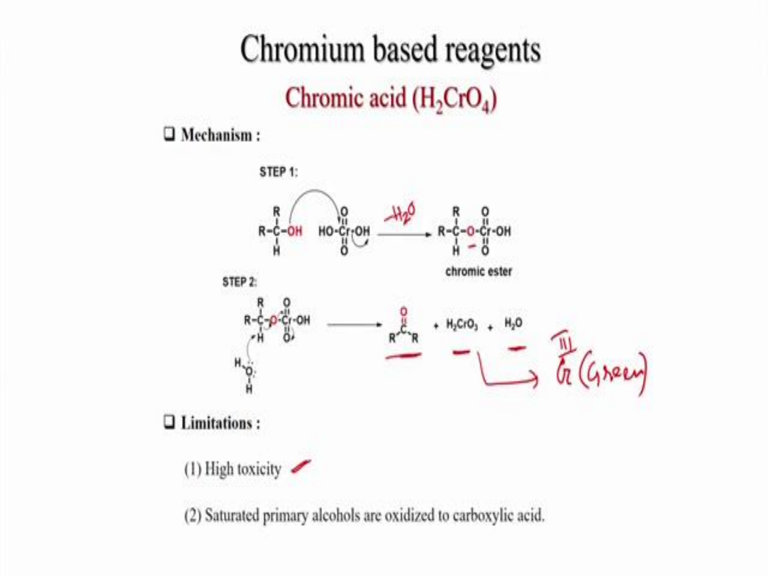

Chromium based reagents

Chromic acid (H_2CrO_4)

❑ **Mechanism :**

❑ **Limitations :**

(1) High toxicity

(2) Saturated primary alcohols are oxidized to carboxylic acid.

And what is the mechanism of this reaction? So, we can discuss the mechanism that this is very strong acid. So, H_2O liberation is not a problem here. So alcohol first reacts with chromium and then H_2O will liberate and you get the chromic ester. As you can see this oxygen is here, so this oxygen is binding to chromium now. So, this is chromic ester now and this, now the water can take this CH proton and then this CrO will liberate and you get the ketone, H_2CrO_3 and H_2O. And H_2CrO_3 this is plus 4, as I told, this will go to, this goes to chromium 3 ultimately and which is green in colour.

So if you see the colour change in the reaction then also you can understand the reaction is happened. So this plus 4 will goes to plus 3 and you can get the green colour. However it has limitation, like it is highly toxic and it is quite reactive, so we have to be careful. And saturated primary alcohols are oxidised to carboxylic acid. So that we have seen, you cannot control up to aldehyde. So, scientists thought to prepare mild oxidising reagent instead of chromic acid.

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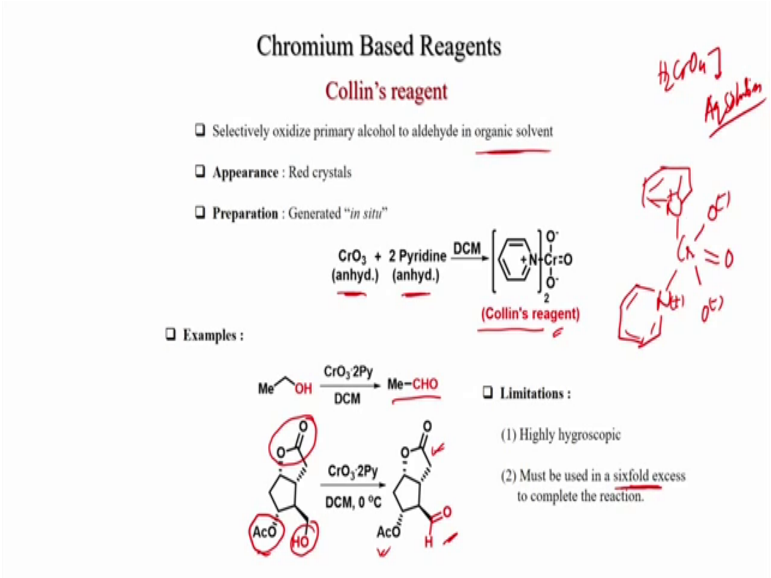

Chromium Based Reagents

Collin's reagent

- ☐ Selectively oxidize primary alcohol to aldehyde in organic solvent
- ☐ **Appearance** : Red crystals
- ☐ **Preparation** : Generated "*in situ*"

- ☐ **Examples :**

- ☐ **Limitations :**

(1) Highly hygroscopic

(2) Must be used in a sixfold excess to complete the reaction.

And first reagent that was developed is Collin's reagent that is the scientist's name and this one, this reagent can selectively oxidise primary alcohol to aldehyde in organic solvent. So that is also important. Earlier we have seen that H_2CrO_4 you have to use aqueous solution. So that is a problem if your compound is not soluble then also it is difficult. So, here you can do an organic solvent. And it has appearance- red crystals. It also generally prepared in-situ. And how you prepare?

Chromium trioxide, you have to take 1 equivalent and 2 equivalent pyridine in anhydrous condition in dichloromethane solvent and then you can get this Collin's reagent. And if you see the structure, actually the pyridine has direct bond with chromium. So chromium one pyridinium and another pyridinium; total 2 pyridinium and now, this O minus, O minus and O. So here also plus 6 but 2 pyridine is there and that's why the reactivity is decreased.

And under this condition, if you take the chromium trioxide 2 pyridine dichloromethane in-situ generate the Collin's reagent and it can selectively oxidise ethanol to acetaldehyde and there is no observation of further oxidation to acetic acid. Also it has been used that, when you have a multi- functional group like acetate group is there, lactone motif and primary alcohol is there and if you put Collin's reagent, in-situ it is prepared and then it found that these 2 groups are undisturbed. So, acetate group is undisturbed.

Acetate, generally is hydrolysed under basic conditions also lactone can be acid or base condition. So, this tells that this is a mild oxidising agent which selectively oxidise primary alcohol to aldehyde. However, there are some drawbacks like this is highly hygroscopic. So, you have to be careful, it has to be anhydrous condition. And must be used in sixfold excess, this is also a drawback of this reagent. You need sixfold excess to complete this reaction.

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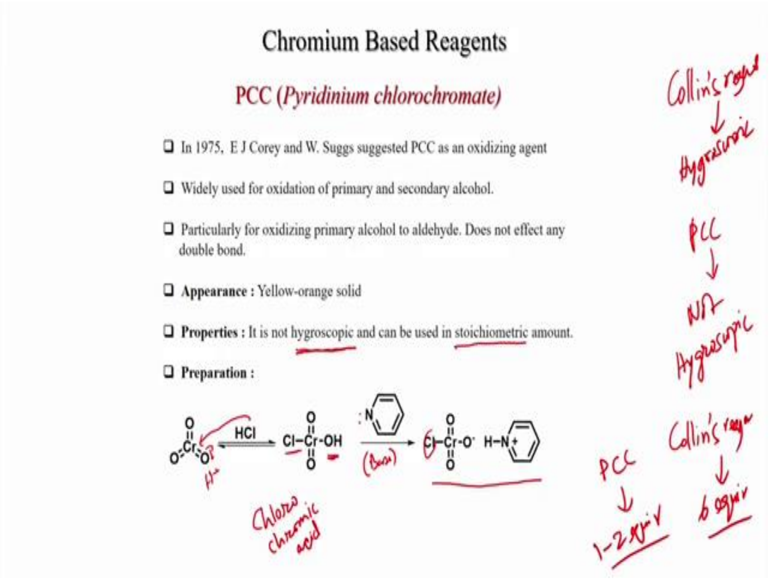

Chromium Based Reagents

PCC (*Pyridinium chlorochromate)*

☐ In 1975, E J Corey and W. Suggs suggested PCC as an oxidizing agent

☐ Widely used for oxidation of primary and secondary alcohol.

☐ Particularly for oxidizing primary alcohol to aldehyde. Does not effect any double bond.

☐ **Appearance :** Yellow-orange solid

☐ **Properties :** It is not hygroscopic and can be used in stoichiometric amount.

☐ **Preparation :**

So, scientists thought then other reagent and one reagent which came after is PCC. This is called Pyridinium chlorochromate. In 1975, E J Corey, Nobel prize winner who developed and W. Suggs developed this reagent as an oxidising agent. And, this is widely used for oxidation of primary and secondary alcohol, particularly for oxidising primary alcohol to aldehyde and it has been found, it does not affect the double bond. So, this is important, that this is not strong oxidising agent. Appearance: yellow-orange solid and properties it is not hygroscopic. So, that is important. Earlier, we have found that Collin's reagent is hygroscopic, but PCC is not hygroscopic. So, this is very important. Also, it can be used in stoichiometric amount. So, this is also important.

In case of Collin's reagent, you have to use 6 equivalent. But in PCC you can use 2 equivalent also, is enough or 1 to 2 equivalent, you can use and you can get the conversion. So, how is it prepared? Chromic acid, chromium trioxide you have to use HCl, and then this Cl minus, first this H plus, is attacking the chromium trioxide and you get the H plus here. Your Cl minus will attack here, and you get this Cl. So, Cl chromium bond is forming. So, this is chloro chromic acid. And now there is OH is there, the acidic H plus, so that will be taken by the pyridine because pyridine is base so, it will take up this proton and you get this salt. So, this is called pyridinium chlorochromate. Pyridinium is there, chloro is there and this is the chromate. So, this is the pyridinium chlorochromate. This way you can prepare. Also, this reagent is commercially available.

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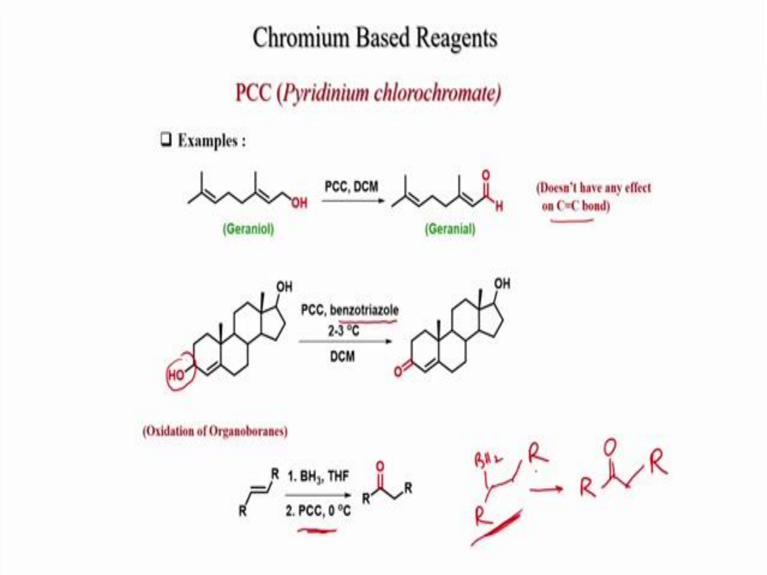

Chromium Based Reagents

PCC (*Pyridinium chlorochromate*)

❑ Examples :

(Doesn't have any effect on C=C bond)

(Oxidation of Organoboranes)

So, as I told that it is mild reducing agent and it does not affect the CC bond. So, this is very important that if you have a alpha beta unsaturated allylic alcohol like this, allylic alcohol it will generate the alpha-beta unsaturated aldehyde selectively and it does not disturb the double bond in the molecule. Similarly, secondary allylic alcohol also can be oxidised to the enone here. Selectively, this alcohol is getting oxidised under PCC and you have to add benzotrizole as an additive and under this condition you get good conversion of the steroid molecule. Also, oxidation of organoborane, so we know that hydroboration reaction of olefin can be carried out to get this borane. So, here you get this BH$_2$, and this BH$_2$ can be oxidised by PCC to get this ketone. So, here, this is the usefulness of PCC that organoboranes can be oxidised also. So, this can be done. First, the double bond will be done hydroboration to get the borane species and then the PCC oxidisation can generate the ketone.

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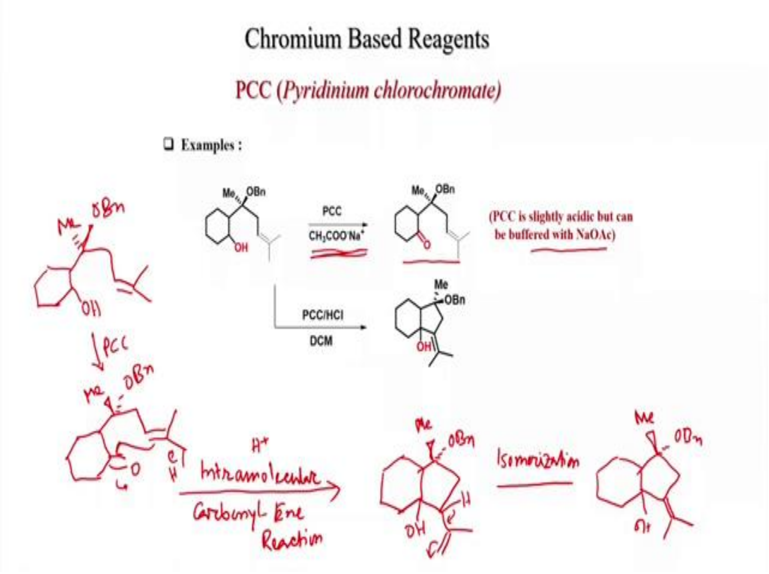

Chromium Based Reagents

PCC (*Pyridinium chlorochromate*)

❑ Examples :

(PCC is slightly acidic but can be buffered with NaOAc)

Also, one thing that we should know that PCC is, it is slightly acidic. So, when there is an external, there is a double bond, which is quite farther under acidic condition, it can create problem. So, you have to add this sodium acetate buffer. And this sodium acetate buffer has been found to be good when you have acid sensitive group. So, here, if you add the sodium acetate buffer, then only you get the desired ketone otherwise, some more reaction will happen. As we can see now, if you add PCC, HCl, DCM then you get this compound. This compound, we can think that how it is forming, so here some more thing is happening. You can see that what is going on.

Now, first the oxidation will happen, then the carbonyl ene reaction will happen and then rearrangement of the double bond will occur to get this compound. So, we can draw the mechanism here. So first PCC you get the ketone. Now, this will undergo, under acidic condition intra-molecular carbonyl ene reaction. So if you put H plus, because you have HCl here so what will happen? So, 5 member ring will form here and you get this one; this terminal olefin first. Now the isomerisation will happen, because this internal olefin is more stable, so you get this compound. So, if you want to stop undesired transformation then you have to use buffers like sodium acetate and then you can get the desired transformation.

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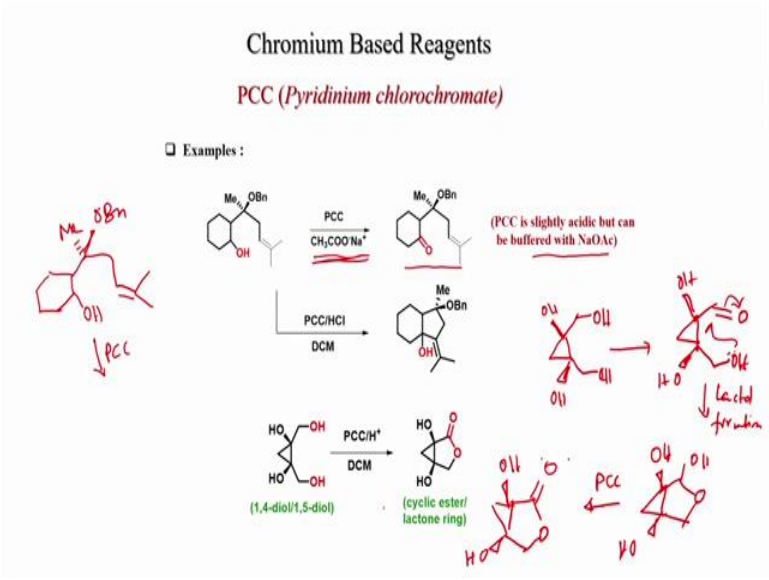

Chromium Based Reagents

PCC (*Pyridinium chlorochromate*)

- ❑ Examples :

(PCC is slightly acidic but can be buffered with NaOAc)

(1,4-diol/1,5-diol)

(cyclic ester/ lactone ring)

Yes, if you have diol like this then you get the product lactone. So, this is also important that if you have an acidic condition, this diol selected will be giving the lactone. So, what is happening here; so as you can see alcohol is oxidising to aldehyde and then the hemiacetal is forming, OH is attacking to the aldehyde, hemiacetal and that will oxidise. So, let us see what is happening here. Yes, so under acid condition what will happen; this OH will attack to this. So, hemiacetal or lactol will form; Lactol formation. Yes, and now this one again PCC, so lactol will be oxidised to lactone. So, that is why in situ, we can generate, in one shot you can generate this lactone.

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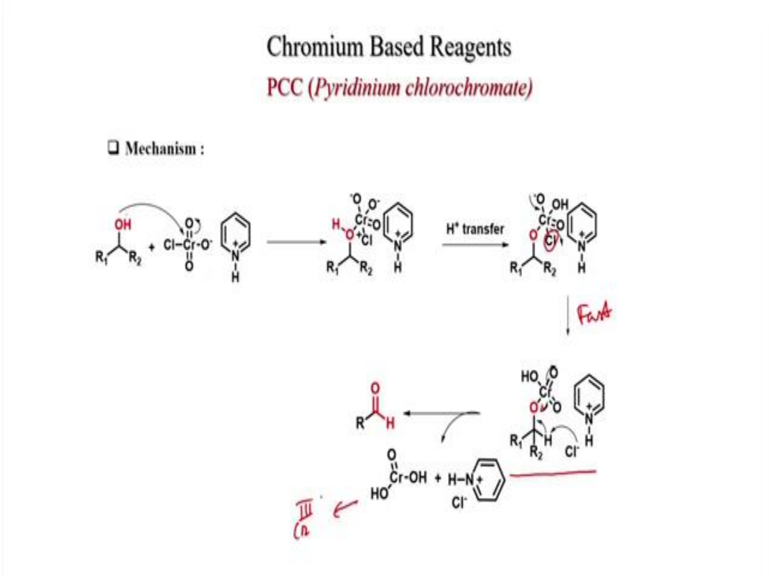

Chromium Based Reagents

PCC (*Pyridinium chlorochromate*)

- ❑ Mechanism :

Okay, there are some more reactions, PCC can perform like, okay, let us discuss first mechanism of this reaction. So, what is happening first. First this OH; OH is attacking to the chromium of this pyridinium chlorochromate and you get this intermediate and now the H plus transfer and you get this chromate ester. And now this is very important because this chloride is good leaving group this chromate ester formation will be very fast and that is what it has been found that, chlorine is very important here because chlorine is a good leaving group.

So this process will be very fast. The elimination of chlorine minus here; it will be very fast and you get this chromate ester and now Cl minus is also a base, so it will abstract proton here and then this chromium O bond will break and you get this aldehyde chromic acid, sorry chromous acid and pyridinium HCl and chromous acid will also be converted to Chromium 3. So, this is the mechanism and we will see some more reactions of pyridinium chlorochromate.

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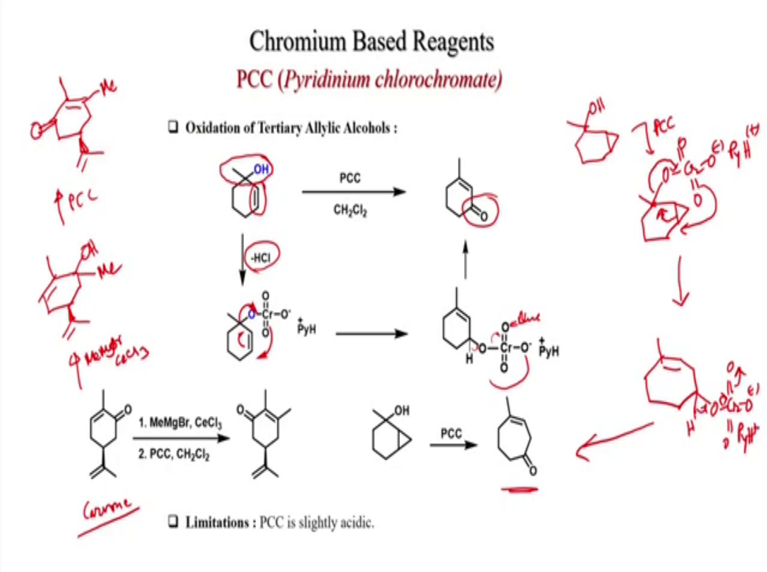

Chromium Based Reagents

PCC (*Pyridinium chlorochromate*)

❑ **Oxidation of Tertiary Allylic Alcohols :**

❑ **Limitations :** PCC is slightly acidic.

One important reaction that has been found that it can oxidise tertiary allylic alcohol. So, this is tertiary alcohol and also, this alcohol is allylic because there is a double bond in the allyl position. And, what has been found is that is if you put PCC under this condition then you get rearrangement. The double bond rearranges to here and OH this carbonyl group is installed in this position. So, this is very useful reaction and the many natural product synthesis this reaction has been utilised. So, what will be the mechanism of this reaction?

So, first as I told you that chlorine is a good leaving group and here we can write in one step also that chromate ester is forming after HCl elimination. Now there will be 3,3 kind sigmatropic rearrangement. So, this oxygen, carbonyl chromium oxygen is attacking here. This double bond is migrated and this blue oxygen is coming to the chromium double bond. Cr-O double bond is forming and after this rearrangement, you get this double bond is here and this oxygen has come here and this might be blue oxygen.

So, this chromate now is formed and this oxygen has come in the allylic position and this as you can see, that all chromium 6 oxidation that this is happening. So, you get the elimination here and ultimately the chromate ester will eliminate to get this enone. And here also as you can see this is carvone. Carvone, if you put methylmagnesium chloride, cerous chloride, what will form? Cerous chloride is a Lewis acid. It will activate this carbonyl and you get this 1, 2 additions selectively. Yes.

So, now you can see this is a tertiary allylic alcohol and because there is a double bond in the allylic position so, what will happen under this PCC condition? PCC condition as you have seen this allylic position, the carbonyl is coming and double bond is migrating to here so the product we can write like this. Here, the methyl group here, another methyl and a new carbonyl group will come. So, this will be the product. Yes.

If in the allylic position, if you have the cylopropane group, then this ring expansion happens. We can also discuss the mechanism that here what happen, this also tertiary allylic alcohol. So, if you give PCC then you get this chromate ester formation. Now what will happen, now this oxygen will come here and this bond will break and this will come to here. So, ultimately you will get ring expansion. Ring expansion here, the double bond is there and now here you have the OCR, O, O, O minus.

Now as you have seen, this will be taken by pyridinium and this chromium H_2CrO_3 will liberate, H_2CrO_3 pyridinium will liberate and you get this cyclopentanone, sorry cycloheptanone. So, when we have a tertiary allylic alcohol with a cyclopropane group, then this ring enlargement is possible. So, as we have seen that this is a limitation of PCC. PCC is slightly acidic and there might be some side reaction when there is an external double bond. So, in that case, all acid level group, so in that case, you have to use sodium acetate buffer.

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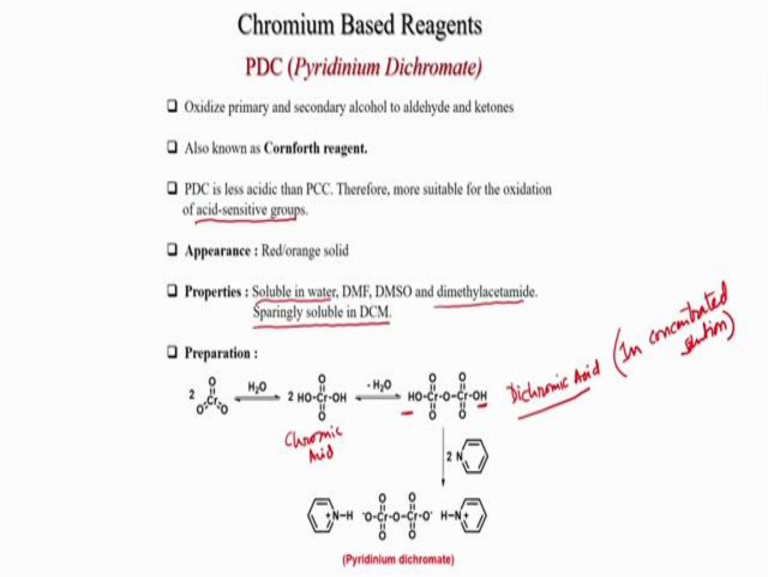

Chromium Based Reagents

PDC (*Pyridinium Dichromate)*

- ☐ Oxidize primary and secondary alcohol to aldehyde and ketones
- ☐ Also known as **Cornforth reagent.**
- ☐ PDC is less acidic than PCC. Therefore, more suitable for the oxidation of acid-sensitive groups.
- ☐ **Appearance :** Red/orange solid
- ☐ **Properties :** Soluble in water, DMF, DMSO and dimethylacetamide. Sparingly soluble in DCM.
- ☐ **Preparation :**

(Pyridinium dichromate)

So, that is why in scientists understood that there should be less acidic reagent and that is why PDC was discovered. PDC is Pyridinium dichromate. This oxidise primary and secondary alcohol to aldehyde and ketones. Also it is known as Cornforth reagent, that was the scientist’s name. PDC is less acidic than PCC therefore, more suitable for the oxidation of acid-sensitive groups. So, it is very important. Also its appearance is red-orange solid. It is soluble in water, DMF, DMSO and dimethylacetamide and sparingly soluble in dichloromethane whereas, PCC oxidation is generally carried out in DCM but PDC, you can use DMF as well as DCM both also in water.

How is it prepared? So, chromium trioxide, aqueous solution of chromium trioxide is generally giving chromic acid and which can generate the dichromic acid. This is dichromic acid and it has been found that if it is concentrated solution, then the chromic acid converts to dichromic acid more actually. So, this equilibrium is, on the right side when there is a very concentrated solution of chromium dioxide; in concentrated solution. So a concentrated solution of chromium trioxide has to be prepared and then pyridine has to be added. And pyridine 2 equivalent of pyridine is consumed here because there are 2 acidic protons and then you get this pyridinium dichromate salt and you can filter it. So, as you can see there is no Cl minus is there so, it is actually no HCl acid is used. So, this is a neutral compound.

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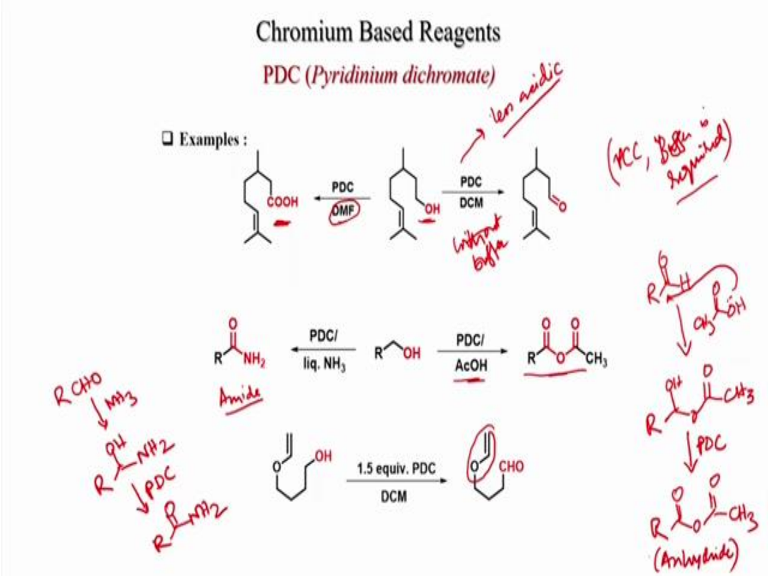

Chromium Based Reagents

PDC (*Pyridinium dichromate*)

❑ Examples :

And it has been used that if here, this kind of alcohol, there is another double bond is there, we have found that in PCC condition we have to use the buffer but in PDC condition, you can use without buffers. So, this is very important without buffer you can oxidise but, for PCC buffer is required. Otherwise, as we have seen that carbonyl any kind of reaction will happen so, PCC condition we have to use the buffer. But PDC, it is not so acidic, so this proves that PDC is less acidic than PCC. This reaction proves that there is not undesired transformation happen when we use the PDC. Also, this is special about PDC that in DMF condition, it becomes more oxidising agent, means its oxidising power increases and it oxidise alcohol to carboxylic acid. This also is used very much in natural product synthesis, PDC and DMF.

Also, when under condition acetic acid is used then this anhydride formation is observed. So, here we can see that ROH first goes to RCHO and then acetic acid is coming. So, this anhydride will form. So, once we can convert an alcohol to acetate anhydride, acetate group containing anhydride by treatment with acetic acid. Similarly if you put PDC in liquid ammonia, you can get the amide. So, here also first the aldehyde will form and then this can give to amine also, but here we get selectively the amide, under PDC condition. Also, this kind of enol ether compound, this is very acid sensitive because if you put PCC this will give side reaction but here it has been found that if under PDC condition it selectively oxidise to the aldehyde and this moiety is untouched. So, this is very important, when you have acid sensitive group, you can use PDC without using buffer and you can get the desired conversion.

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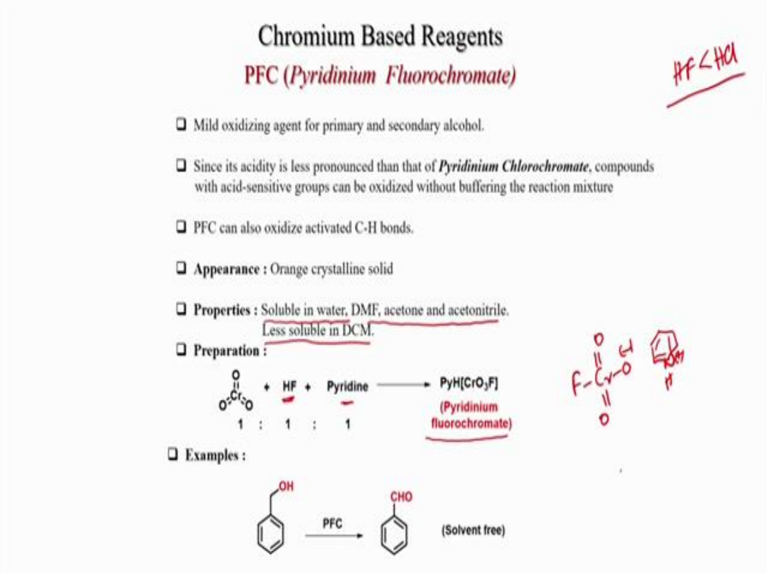

Chromium Based Reagents

PFC (*Pyridinium Fluorochromate*)

HF < HCl

- ❑ Mild oxidizing agent for primary and secondary alcohol.
- ❑ Since its acidity is less pronounced than that of ***Pyridinium Chlorochromate***, compounds with acid-sensitive groups can be oxidized without buffering the reaction mixture
- ❑ PFC can also oxidize activated C-H bonds.
- ❑ **Appearance :** Orange crystalline solid
- ❑ **Properties :** Soluble in water, DMF, acetone and acetonitrile. Less soluble in DCM.
- ❑ **Preparation :**

- ❑ **Examples :**

Another reagent which was discovered which is Pyridinium Fluorochromate and this is also mild oxidising agent for primary and secondary alcohol and since its acidity is less pronounced than that of pyridinium chlorochromate, because HF is a weaker acid than HCL, so pyridinium fluorochromate is also less acidic. So, compounds with acid sensitive groups can be oxidised without buffering the reaction mixture. So, as we have observed like in PDC, you do not need the buffer, in pyridinium fluorochromate also you do not need the buffer. So, it is less acidic.

Another important reaction that PFC undergoes is the oxidation of the activated CH bonds. Its appearance is orange crystalline solid and it is soluble in water. This has also wide solubility. It is soluble in water, DMF, acetone and acetonitrile. Less soluble in DCM like PDC. It can be prepared by chromium trioxide 1 equivalent HF 1 equivalent, and pyridine 1 equivalent and you get this pyridinium fluorochromate salt. So, it is like as you have seen, for pyridinium fluorochromate, so the structure will be similar. So, this is a pyridinium flourochromate. It has been found that reactions can be performed also under solvent free conditions, like benzyl alcohol is oxidised to benzyldehyde under solvent free condition.

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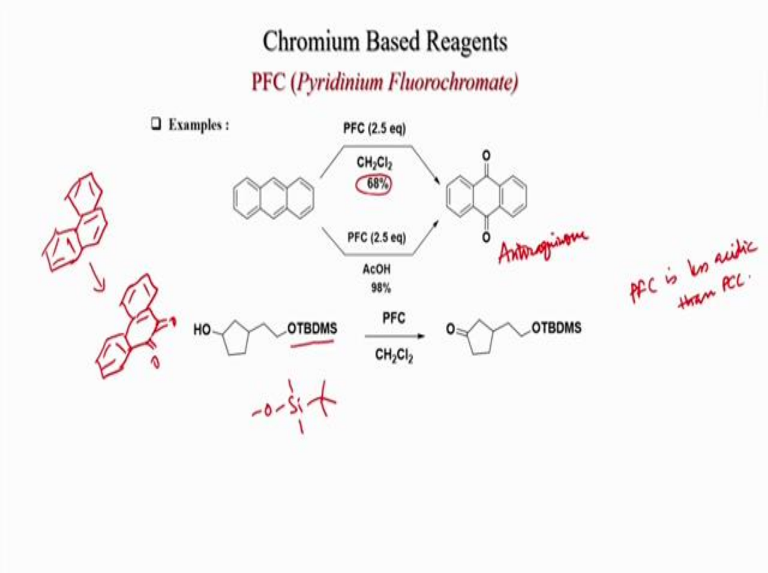

Chromium Based Reagents

PFC (*Pyridinium Fluorochromate)*

❑ Examples :

PFC is less acidic than PCC.

And this is also a very important reaction that PFC only undergoes oxidation of anthracene and also phenanthrene can be oxidised. This is anthraquinone. Also, phenanthrene can be oxidised to phenanthroquinone. And it has been found that in this reaction if acetic acid is used along with PFC, then this yield is enhanced. So earlier 68 percent was obtained and now under acetic acid, the solvent you get 98 percent. So, it tells that if you use acid in this reaction, then the yield gets enhanced.

Also, it has been found that if it is a acid sensitive group like OTBDMS, this is actually, O Silyl 2 methyl group is there, dimethyl tertiary butyl, dimethylsilane. So, this group is acid sensitive and under PCC condition, this group might get also deprotected. But under PFC condition, you can protect this primary alcohol and selectively oxidise this secondary alcohol. So that, it takes that PFC is less acidic than PCC.

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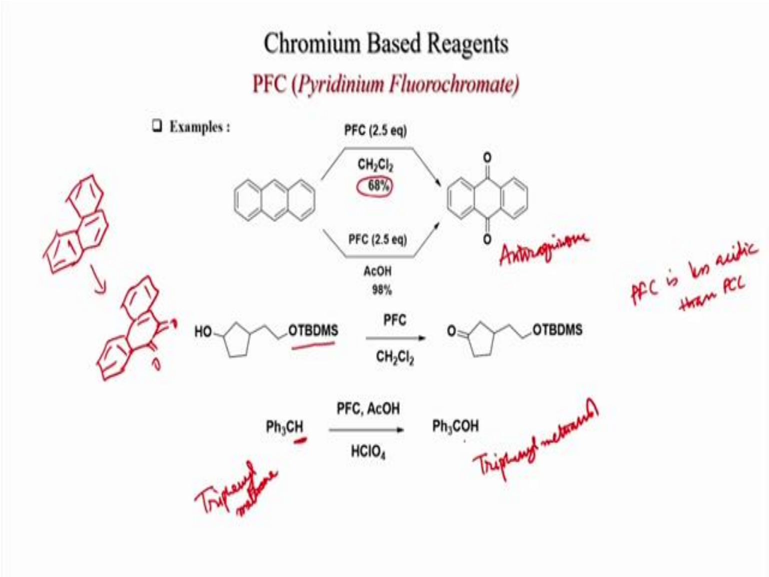

Chromium Based Reagents

PFC (*Pyridinium Fluorochromate*)

❑ Examples :

Also, triphenyl methane, under PFC acetic acid, chloric acid condition, you can generate triphenyl methanol. So, this is very important that benzylic CH gets activated here. This is benzylic CH and this gets to the alcohol.

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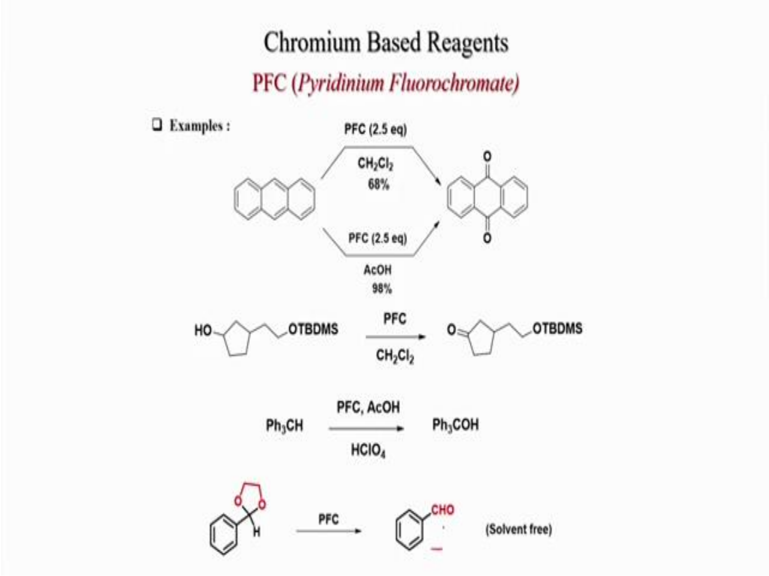

Chromium Based Reagents

PFC (*Pyridinium Fluorochromate*)

❑ Examples :

It has been found that if you have an acetal motif, then PFC can oxidise, means PFC can hydrolyse this acetal motif and it can generate the aldehyde. So, this also tells that PFC is not very acidic but it is; it can do the hydrolysis of the acetal to get the benzaldehyde.

So, today we have learnt different chromium based oxidising reagents like chromic acid which is very strong, which is generally aqueous solution is used then we have seen the Collin's reagent. Collin's reagent you can use in organic solvent and this was first developed that it can be used organic solvent and it is mild. It can selectively oxidise primary alcohol and secondary alcohol to aldehydes and ketones. Earlier chromic acid only, you cannot control, with primary alcohol, secondary alcohol. Secondary alcohol gives ketone but primary alcohol gives the carboxylic acid.

So, one problem with Collin's reagent was it was hygroscopic so it cannot be utilised tremendously that is why PCC reagent was discovered. And PCC, it is slightly acidic, but because of chlorine is there, the chromate ester formation is very facile and it can be used also not in the truly moisture free condition, you can have some moisture also, so this reaction does not hamper and the products are also selectively formed when PCC under buffer is used because it is slightly acidic, so we can control the acidity by using buffer like sodium acetate and you can got the desired transformation.

Also, PCC undergoes tertiary allylic alcohol oxidation and the rearrangement happens you have seen the alpha beta unsaturated ketone is formed with a double bond arrangement. Then, because PCC was acidic so PDC was discovered which is pyridinium dichromate and which has been found to be neutral. So, earlier when acid sensitive group was used, PCC must be used with buffer but here without buffer also PDC can oxidise the alcohol in presence of acid sensitive group.

Then PFC was developed, PFC was also found to be less acidic than PCC and defined oxidation can be carried out also with PFC, anthracene, and phenanthrene can give anthraquinone, phenanthraquinone. Also, benzylic CH bonds can be also oxidised. We have also seen triphenyl methane under acidic condition in PFC gives the triphenyl methanol. So, we have seen, different chromium reagents with their various reactivity and selectivity. So, I hope you have enjoyed. Thank you.