Reagents in Organic Synthesis
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Lecture 02: Non Metal Based Reagents for Oxidation

Key words: Etard reaction, Parikh oxidation, Swern oxidation, Corey-Kim oxidation

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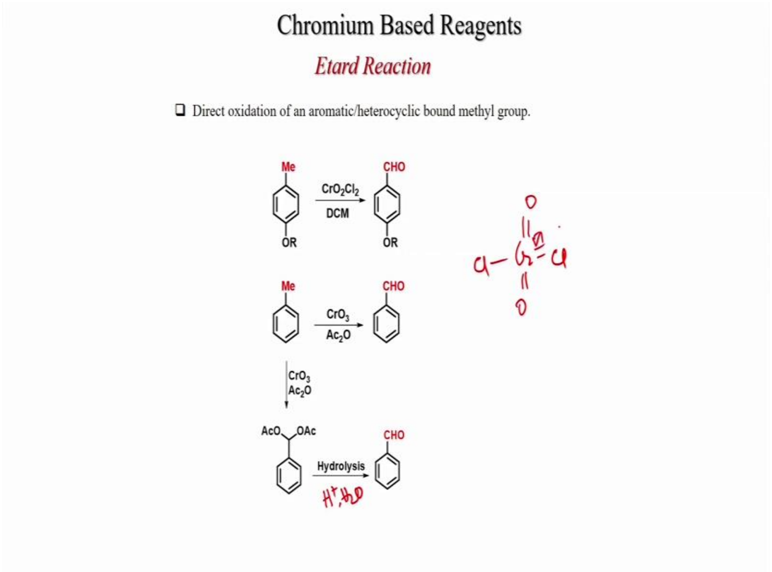

Chromium Based Reagents

Etard Reaction

❑ Direct oxidation of an aromatic/heterocyclic bound methyl group.

Welcome again. Today we will teach Etard reaction, and also DMSO based oxidation reaction. So, first we will discuss Etard reaction. Etard reaction is the direct oxidation of an aromatic or heterocyclic bound methyl group to aldehyde group. Like here, toluene derivative is oxidized with chromyl chloride to the bezaldehyde derivative. And, you have to use DCM solution, because otherwise, the reaction is very vigorous and under this condition, toluene derivative can be oxidized to benzaldehyde derivative.

Also, there is another reagents chromium trioxide and acetic anhydride mixture, can also oxidize toluene derivative to benzaldehyde. Here, the chromium trioxide acetic anhydride, generate this diacetoxy derivative, and which after acidic hydrolysis; can generate the benzaldehyde derivative. And, if you see the chromyl chloride structure, this is like this. Here also, if you consider the oxidation number this plus 6 also.

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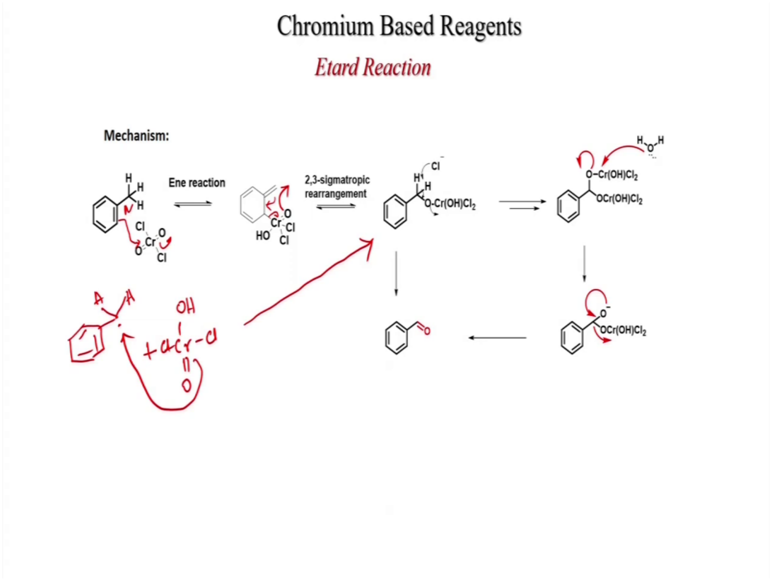

Chromium Based Reagents

Etard Reaction

Mechanism:

And now, we will discuss the mechanism of this reaction. There are two well accepted mechanism. First is the ene. So, here the toluene derivative; and this the chromyl chloride. First this ene type reaction can happen, to generate this chromium compound. And, this chromium compound, then can undergo 2, 3sigmatropic rearrangement, like this; this is 2, 3sigmatropic rearrangement, because the 5 atoms, 1, 2, 3, 4, 5; 5 atoms are in bond and then, you get this (comp) alkoxy chromium compound.

And, this compound, this, this acidic hydrogen, can be deprotonated by Cl minus and this chromium can be withdrawn from the compound to give this benzaldehyde. Alternately there are, again this possibility, further in reaction, and sigmatropic reagent, which can generate this acetyl derivative and which, can react further with water. Suppose, water reacts with chromium, here and then this alkoxy compound is formed, which after elimination, can give the benzaldehyde.

So, here just I will tell the another mechanism, which is possible and which was earlier proposed by the authors that this kind of benzylic radical can formed and here this, then this can react, to this radical and which will form this intermediate. So, either by radical possibility or via ene mechanism, we will generate this alkoxy chromium intermediate, which after hydrolysis of further reaction, this acetyl chromium complex and they will also, give the benzaldehyde.

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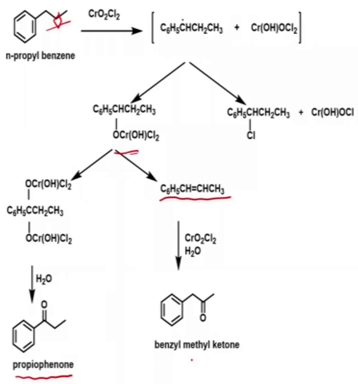
Chromium Based Reagents

Etard Reaction

- ☐ **Limitations:** Multiple products formed



However, there are limitations for this reaction. One limitation is the multiple products will form, when you increase the chain length. Like, if you use n-propyl; instead of methyl, there are n-propyl group, then there are many products formed. And, if we consider the radical mechanism here the benzylic radical will form, and this will be by-product. And now, this radical can react again, to give this compound, a chromium complex, as well as chlorine can reacts to give this chlorine compound. This was also, side product of this reaction.

Now, this one as we discussed earlier, this can further react with chromyl chloride to generate this acetyl chromium complex, which after hydrolysis generate the desired product. So, this is the desired product that the benzylic CH is getting activated, and it goes to the carbonyl compound. So, this ketone is formed. However, there is also possibility, for the elimination reaction to generate this olefin. And, this olefin further react with chromyl chloride, and after hydrolysis, can generate this benzyl methyl ketone, have the; this carbon is activated. And, you get the ketone, which is benzyl methyl ketone here.

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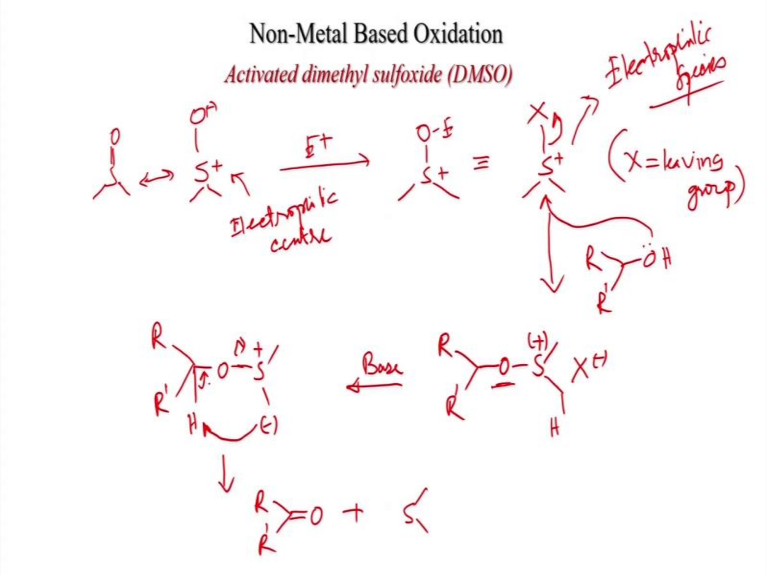
Non-Metal Based Oxidation

Activated dimethyl sulfoxide (DMSO)



Now, we will discuss DMSO based oxidation, activated dimethyl sulfoxide. As you know, DMSO is used as the solvent in the lab but it has also used oxidizing reagent; so, that we can discuss now. So, DMSO. So, this will be resonance. So, DMSO can resonating form like this one. And, this an electrophilic; so, this is an electrophilic center.

And, that is why the scientists thought, that alcohol can be reacted at this electrophilic center. For that; since O minus is a leaving group this group has to; has to be modified. And that is why, they reacted first this one with electrophile, which gives you this electrophile, which we can write S plus X, where X will be, actually a leaving group, leaving group.

Now, if you react with alcohol having R R dash, this sulphenate salt is formed; actually, X minus can be there, here. Now, reaction with base. So, base what it does? It can either activate this one. It can generate negative charge. And then, it can form this, ketone, and you get DMS; DMS.

So, dimethyl sulfoxide, ultimately is going to dimethyl sulphide. So, it is getting reduced. And, if you consider carefully, this alcohol OH; alcohol OH, actually here, it is reacting, as a nucleophile. And, so, the main strategy, that you generate this electrophilic species. So, main electrophilic species and then you have to react with alcohol. And also, you have to use a base, which will deprotonate this or this; ultimately carbonyl compound will form and dimethyl sulphide will be a byproduct.

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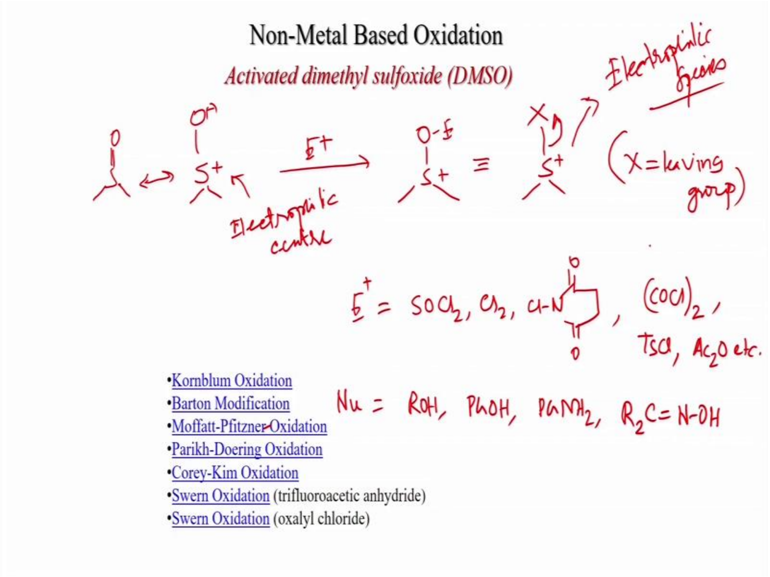

Non-Metal Based Oxidation

Activated dimethyl sulfoxide (DMSO)

- Kornblum Oxidation
- Barton Modification
- Moffatt-Pfitzner Oxidation
- Parikh-Doering Oxidation
- Corey-Kim Oxidation
- Swern Oxidation (trifluoroacetic anhydride)
- Swern Oxidation (oxalyl chloride)

And different electrophilic reagents have been used for this fast reaction with dimethyl sulfoxide. So, that we will write now like electrophilic species can $SOCl_2$, chlorine. It can be N-chlorosuccinimide. It can be oxalyl chloride. It can be tosyl chloride, acetic anhydrate, etc. Also, not only alcohol, this strategy can be used in other oxidation also. Like, normal alcohol, phenol, ainiline, also oxime compound can also be used for (oxidize) oxidation, in this strategy.

And, there are many name reactions, like which we will discuss now, like Kornblum oxidation; because there are different electrophilic reagents can be used. And, that is why different name reaction came out, like Kornblum oxidation, Barton modification of Kornblum oxidation, Moffat Pfitzner oxidation, Parikh Doering oxidation, Corey Kim Oxidation. Swern oxidation, there are two variants. First, developed was with trifluoroacetic anhydride and later they modified with oxalyl chloride, which is called the Swern oxidation; that is what the familiar Swern oxidation is a oxalyl chloride.

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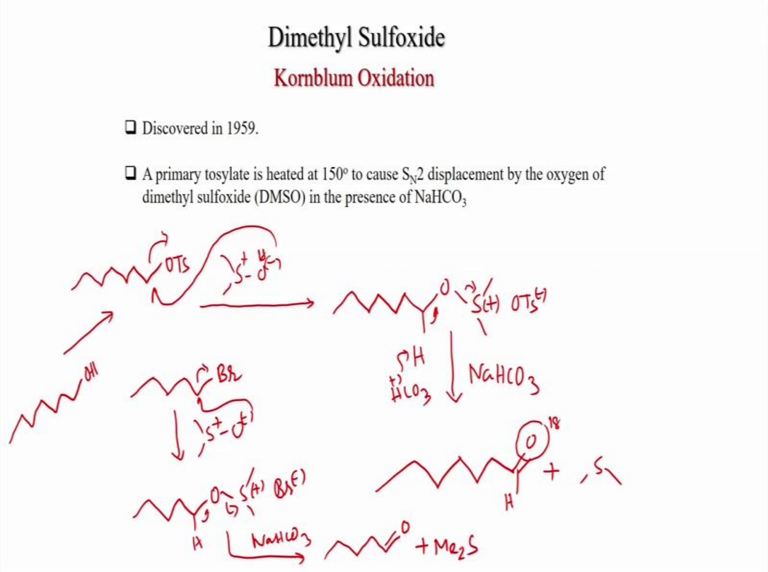

Dimethyl Sulfoxide

Kornblum Oxidation

- ❑ Discovered in 1959.
- ❑ A primary tosylate is heated at 150° to cause S_N2 displacement by the oxygen of dimethyl sulfoxide (DMSO) in the presence of $NaHCO_3$

So, dimethyl sulfoxide mediated oxidation, first we will discuss Kornblum oxidation. This oxidation was discovered in 1959. A primary tosylate is heated at 150 degree centigrade to S_N2 displacement by the oxygen of dimethyl sulfoxide in the presence of sodium bicarbonate. So, this is very harsh condition and we can see an example like this tosylate. And here, this tosylate you can easily obtain from the alcohol – 1, 2, 3, 4, 5, 6, 7 , like heptanal, and then you get the tosylate.

Now, if you heat with DMSO, then you get the displacement and you get this sulphuric salt. Now, if you put sodium bicarbonate, in this sulphuric salt then, this acidic hydrogen this gets deprotonated by the sodium bicarbonate anion. And, you get the aldehyde, and heptanol plus dimethyl sulphide. So, this is an only example. Also, you can see that this oxygen is coming from the DMSO, so if you put this O 18, then this aldehyde, will be O 18.

Also, Kornblum shown that, you can use alkyl bromide also. And, alkyl bromide, similarly with reaction with DMSO, will do an S_N2 substitution, and you get the sulfenate salt. And, now, if you put, sodium bicarbonate; here we have used pentyl bromide. So, if you use sodium bicarbonate, then you get, the elimination of DMS, and you get the aldehyde.

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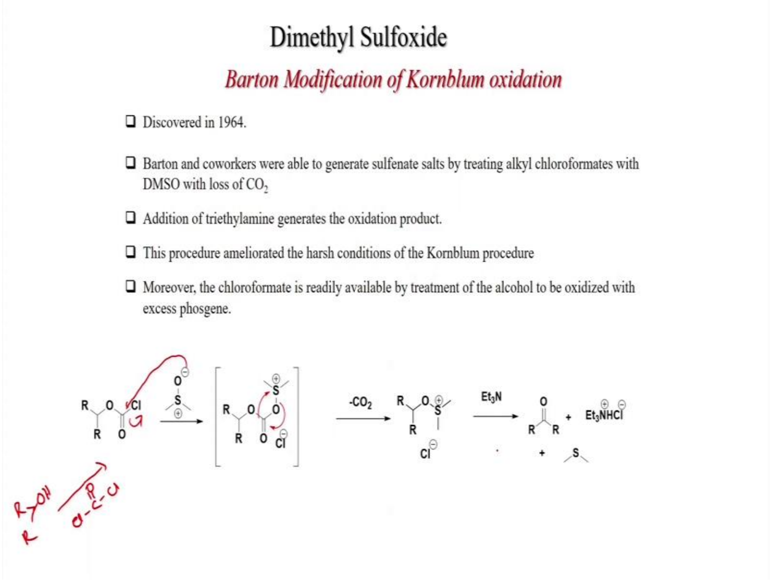

Dimethyl Sulfoxide

Barton Modification of Kornblum oxidation

- ❑ Discovered in 1964.
- ❑ Barton and coworkers were able to generate sulfenate salts by treating alkyl chloroformates with DMSO with loss of CO_2
- ❑ Addition of triethylamine generates the oxidation product.
- ❑ This procedure ameliorated the harsh conditions of the Kornblum procedure
- ❑ Moreover, the chloroformate is readily available by treatment of the alcohol to be oxidized with excess phosgene.

One drawbacks of this reaction, was that, high temperature so, Barton modified this reaction, and Barton discovered this modification in 1964. They were able to generate sulfenate salt by treating alkyl chloroformates with DMSO, with loss of CO_2. Addition of triethylamine; instead of an inorganic base, they use organic base, like triethylamine, which generates the oxidation product.

And, this procedure ameliorated the harsh conditions of the Kornblum procedure. And, the chloroformate is readily available, by treatment of the alcohol to be oxidized with excess phosgene. Here, actually you can, earlier what, you have to make the tosyl derivative; here we have to generate this chloroformate derivative. And, this you can generate easily, by treating with phosgene. So, if you treat with phosgene, the alcohol then, you get this chloroformate.

Now, DMSO reacts; and DMSO reacts, first time to generate this derivative, and now this derivative, you can see this oxygen can be react here and carbon dioxide eliminate. And, after carbon dioxide elimination, we get the sulfenate salt, that was the main electrophilic species, we have seen here. And now, this one, after triethylamine; basic condition, it can generate the carbonate compound triethylammonium hydrochloric salt and dimethyl sulphite.

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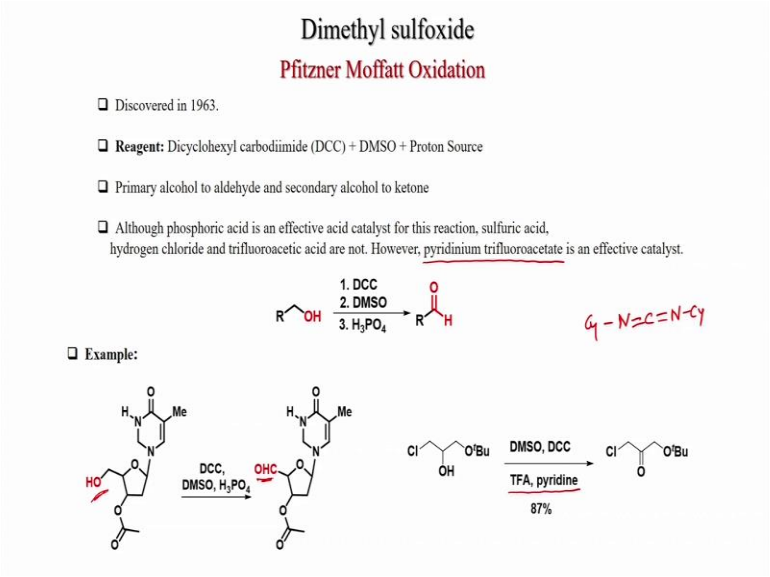

Dimethyl sulfoxide

Pfitzner Moffatt Oxidation

- ❑ Discovered in 1963.
- ❑ **Reagent:** Dicyclohexyl carbodiimide (DCC) + DMSO + Proton Source
- ❑ Primary alcohol to aldehyde and secondary alcohol to ketone
- ❑ Although phosphoric acid is an effective acid catalyst for this reaction, sulfuric acid, hydrogen chloride and trifluoroacetic acid are not. However, pyridinium trifluoroacetate is an effective catalyst.

❑ **Example:**

Now, another oxidation was Pfitzner Moffatt oxidation. It was discovered in 1963. Here, dicyclohexyl carbodiimide, DMSO, and a proton source was used. Primary alcohol can be oxidized to aldehyde to ketone. Although, phosphoric acid; generally phosphoric acid is used, here, the proton source. Phosphoric acid is an effective acid catalyst for this reaction. Sulfuric acid, hydrogen chloride, trifluoro acetic acid; acetic acid are not. However, pyridinium trifluoroacetate is an effective catalyst.

This is the standard condition that DCC, DMSO and H_3PO_4; and DCC. This is the DCC structure dicyclohexyl carbodiimide, DMSO and phosphoric acid. And, under this condition, you can selectively oxidize primary alcohol. So, here if you this complex structure, here you have an acetate group. Here, tetrahydrofuran motive and, these groups are not disturbed. You can selectively, get oxidation of the alcohol to the aldehyde.

Also, you can see, here a leaving group, chlorine, chloride is there and OH, the secondary alcohol is selectively oxidized under this condition. Here, that is what the pyridinium trifluoroacetate actually was used; the mixture of TFA and pyridine. This was also found to be, good proton source. Actually, this is mild compared to phosphoric acid and can give the product.

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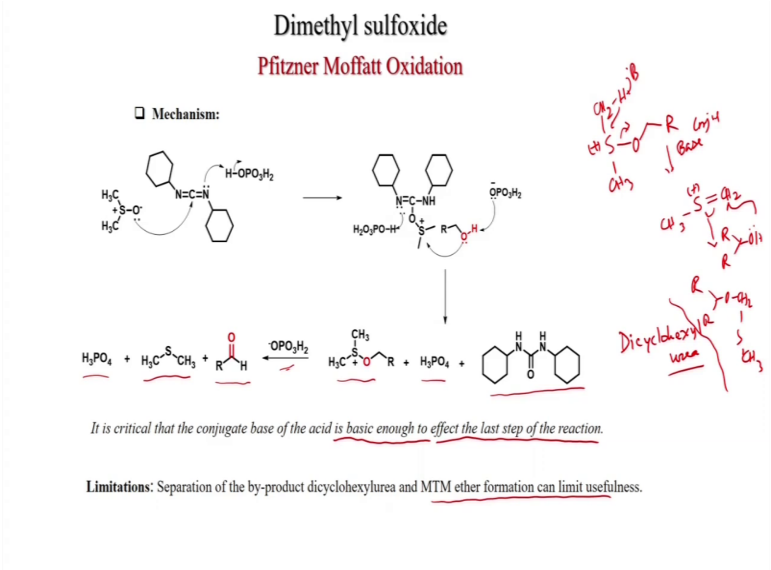

Dimethyl sulfoxide

Pfitzner Moffatt Oxidation

❑ **Mechanism:**

It is critical that the conjugate base of the acid is basic enough to effect the last step of the reaction.

Limitations: Separation of the by-product dicyclohexylurea and MTM ether formation can limit usefulness.

So, what will be the possible mechanism for this reaction? So, DMSO can react first with the DCC. Actually, the DCC has to be activated with an acid. Then only, the DMSO can react. So, DMSO reacts at the carbon atom, and of this diimmide. And, nitrogen is activated by the phosphoric acid. And, you get; after this you get, this intermediate. And now, the alcohol can be considered; it is deprotonated by the conjugate base of the phosphoric acid that is the phosphate.

And, this nucleophilic reaction happens here. And also, this imine bond is activated by the phosphoric acid. And, after that, you get the sulfenate salt, you get phosphoric acid back. And, this is the urea dicyclohexylurea. Actually, this precipitates in the reaction. And, after that, since there is no external base, it is considered that the conjugate base of the acid; conjugate base of the acid, that is the phosphate. It actually, acts as a base and deprotonates here. And, you get the aldehyde, dimethyl sulphide and phosphoric acid back.

So, that is why, it is critical, that the conjugate base of the acid, should be basic enough to effect the last step of the reaction, this is very important. Otherwise, this desired transformation, without base, this sulfenate salt cannot decompose to the aldehyde and dimethyl sulphide. However, there is also drawback of this reaction, like separation of the byproduct, dicyclohexylurea and MTM ether formation can limit its usefulness.

So, this we can discuss now. Actually, if you see this intermediate conjugate base; conjugate base, you get this one. This can be formed also. And, then your alcohol can react here. So, this is a side product. So, that is why the MTM; this is the MTM ether formation. So, this is a side product of this reaction, because under acidic condition, a conjugate base can generate this as sulphonium cation and however, then the alcohol can react to give this ether.

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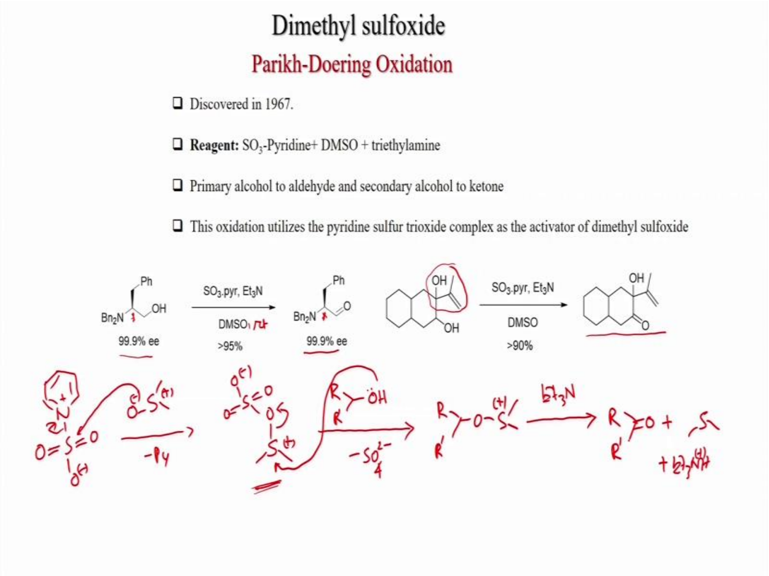

Dimethyl sulfoxide

Parikh-Doering Oxidation

- ☐ Discovered in 1967.
- ☐ **Reagent:** SO_3-Pyridine+ DMSO + triethylamine
- ☐ Primary alcohol to aldehyde and secondary alcohol to ketone
- ☐ This oxidation utilizes the pyridine sulfur trioxide complex as the activator of dimethyl sulfoxide

Another oxidation is Parikh-Doering oxidation. And, here; this compound was discovered in 1967. Here, SO_3 pyridine complex was used. SO_3 pyridine is actually, a electrophilic species, which reacts with DMSO, and triethylamine is the base. Here, primary alcohol to aldehyde, and secondary alcohol to ketone. And, the oxidation utilizes the pyridinium sulfur complex, as the activator of dimethyl sulfoxide.

Here are some examples. So, this reaction is quite mild. As you can see, there is a chiral center here. And, the starting material ee was 99.9 percent ee. And, after this reaction, the aldehyde is formed, but the chiral center is not racemized, under the reaction condition.

Generally, this is room temperature, and under this condition, the enantioselectivity retained.

Here also, there is a secondary alcohol and there is a tertiary allylic alcohol. As we have seen, this species oxidization, this compound can isomerize and give the ketone, enone species. So, under this condition; Parikh-Doering condition, you can get selectively, this secondary alcohol oxidation, without disturbing this. So, this is very important.

And, we can discuss now the mechanism of this reaction. So, this is the SO_3 pyridine complex. Now, DMSO reacts here. So, pyridine is out and now, you get your, this sulfate. So, sulfate 2 minus is the leaving group here. And, after that you get, this sulfenate salt. Actually, here SO_4 2 minus is the anion here.

And now, after treating with triethylamine, you will get the ketone and dimethyl sulphide, and diethyl amine, ammonium salt. So, this is the reaction in all cases that electrophilic sulphur species will be generated. And then, the alcohol will react. And, after elimination, and formation of dimethyl sulphide, you get the aldehyde or ketone.

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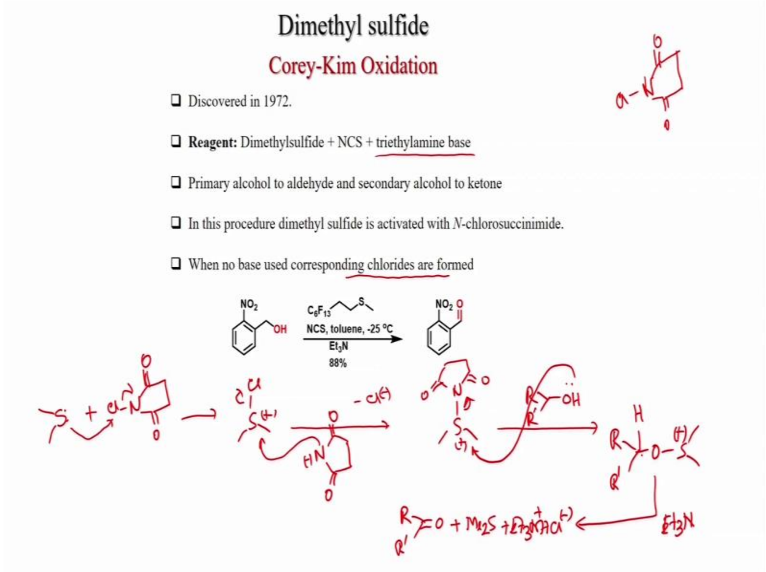

Dimethyl sulfide

Corey-Kim Oxidation

❑ Discovered in 1972.

❑ **Reagent:** Dimethylsulfide + NCS + triethylamine base

❑ Primary alcohol to aldehyde and secondary alcohol to ketone

❑ In this procedure dimethyl sulfide is activated with *N*-chlorosuccinimide.

❑ When no base used corresponding chlorides are formed

Corey group also discovered another reaction, which is called Corey-Kim reaction. And, interestingly he used dimethyl sulfide, instead of DMSO. It was discovered in 1972.

Here, dimethyl suphide, NCS this is *N*-chlorosuccinimide. So, this was used, *N*-chlorosuccinimide, which is also electrophilic species, and triethylamine as the base. Primary alcohol also, gets to aldehyde and secondary alcohol to ketone. In this procedure, dimethyl sulfide is activated with *N*-chlorosuccinimide.

When no base used, corresponding chlorides are formed. So, this is very important. If you do not use, the triethylamine base, then the chloride will form, because chloride also, is a good nucleophile. This is an example. And here, they have used, modified sulphide with a fluorine group. And, under this condition N-chlorosuccinimide, triethylamine, toluene, minus 25 degree centigrade, this nitrobenzyl alcohol is selectively oxidized to the nitrobenzaldehyde.

So, here also we can discuss the mechanism. Here, instead of DMSO, you have dimethyl sulphide. So, dimethyl sulphide first reacts with *N*-chlorosuccinimide. Now, this group can also react; this group succinimidyl group can also react, and generate this compound. Now, alcohol will react. So, this is the intermediate in all our previous reactions and now, triethyl amine. So, if we do not use the base here, then what will happen? This chlorine minus is present here. This chlorine minus can react here and generate the chloro derivative.

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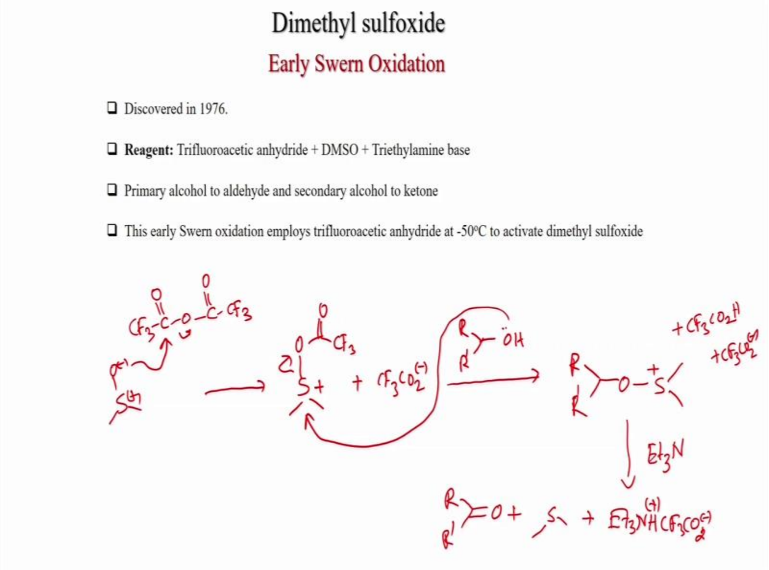

Dimethyl sulfoxide

Early Swern Oxidation

❑ Discovered in 1976.

❑ **Reagent:** Trifluoroacetic anhydride + DMSO + Triethylamine base

❑ Primary alcohol to aldehyde and secondary alcohol to ketone

❑ This early Swern oxidation employs trifluoroacetic anhydride at -50ºC to activate dimethyl sulfoxide

Swern oxidation is a very popular oxidation reaction. So there, Swern first developed a reaction, which is called early Swern oxidation that is discovered in 1976. And here, trifluoroacetic anhydride was used, as the activator, and DMSO as, and diethylamine base. Here also, primary alcohol to aldehyde and secondary alcohol to ketone. This, early Swern oxidation employs trifluoroacetic anhydride, at minus 50 degree centigrade to activate dimethyl sulfoxide.

So, here also we can discuss the mechanism trifluoroacetic anhydride, DMSO. Now, alcohol will, react. Trifluoroacetate is a good leaving group and we get this species. And, you get acetic acid plus CF_3CO_2 minus is there. So, this is the intermediate compound, in all the previous reactions. And now, triethylamine base you get the ketone, dimethyl sulphide and triethyl N plus CF_3CO_2 minus. So, this was the early Swern oxidation.

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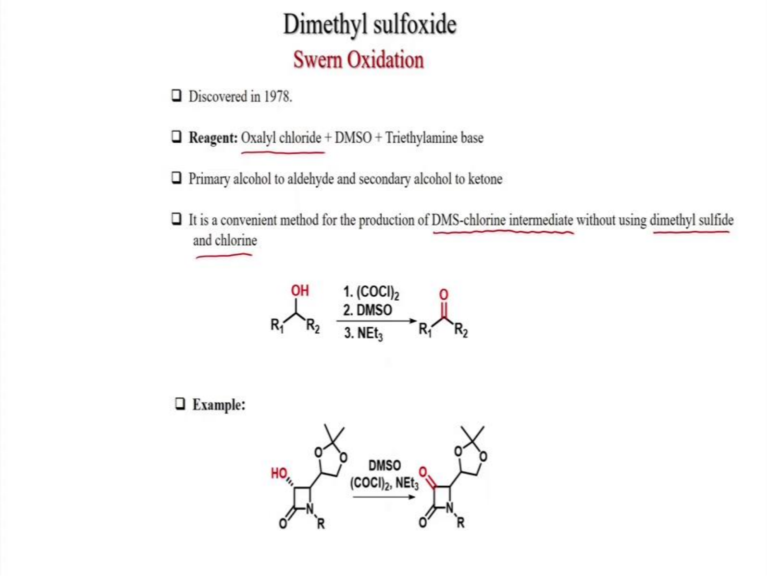

Dimethyl sulfoxide

Swern Oxidation

- ❑ Discovered in 1978.
- ❑ **Reagent:** Oxalyl chloride + DMSO + Triethylamine base
- ❑ Primary alcohol to aldehyde and secondary alcohol to ketone
- ❑ It is a convenient method for the production of DMS-chlorine intermediate without using dimethyl sulfide and chlorine

- ❑ **Example:**

And, later which is common as Swern oxidation, that is, carbonyl; oxalyl chloride as the electrophilic reagent. So, this was discovered in 1978. This is the oxalyl chloride. Earlier was trifluoroacetic anhydride. Here, oxalyl chloride was used, DMSO, triethylamine base. Generally, this reaction occurs at minus 78 degree centigrade. Here also, primary alcohol to aldehyde and secondary alcohol to ketone. It is a convenient method for the production of DMS-chlorine complex, intermediate without using dimethyl sulfide and chlorine.

So, without using dimethyl sulfide and chlorine, we can get this DMS-chlorine complex by oxalyl chloride. This is the standard condition oxalyl chloride, DMSO, triethylamine. Alcohol will covert to the ketone. This is an example, where there are many functional groups. Here, ketone motif is there, here a beta locative motif is there, and you can see, this selectively, the alcohol; secondary alcohol goes to the carbonyl compound.

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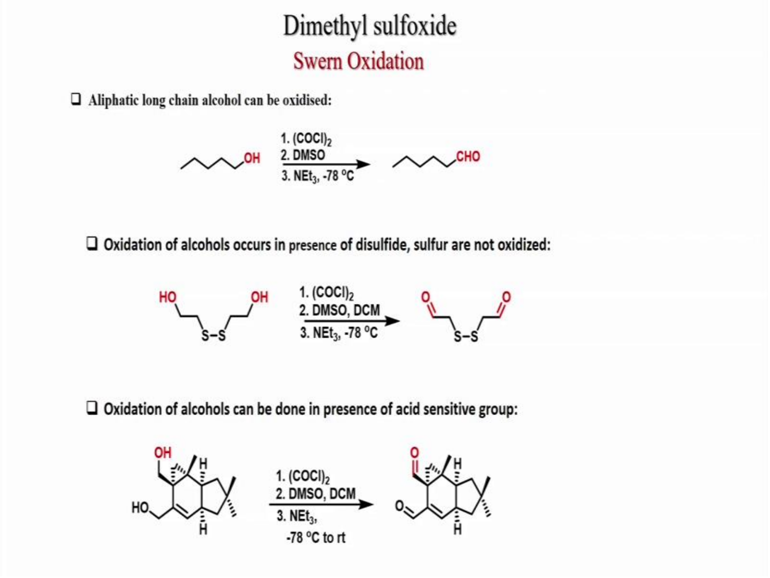

Dimethyl sulfoxide

Swern Oxidation

- ❑ Aliphatic long chain alcohol can be oxidised:
- ❑ Oxidation of alcohols occurs in presence of disulfide, sulfur are not oxidized:
- ❑ Oxidation of alcohols can be done in presence of acid sensitive group:

Here, an aliphatic long chain alcohol was oxidized, with Swern condition oxalyl chloride, DMSO, triethylamine, minus 78 degree centigrade; you get this aldehyde in good yield. Also, in the presence of disulphide, disulphide is prone to oxidation. We know, sulphide once can go leave and also, they can get oxidized to sulfoxide.

But, under Swern condition, this group is intact and selectively, the alcohol group is oxidized to aldehyde. Also, other acid sensitive group, if it is there, like a cyclopropane ring, a double bond, and under this condition, this structure selectively converted to the dialdehyde; without breaking these motives.

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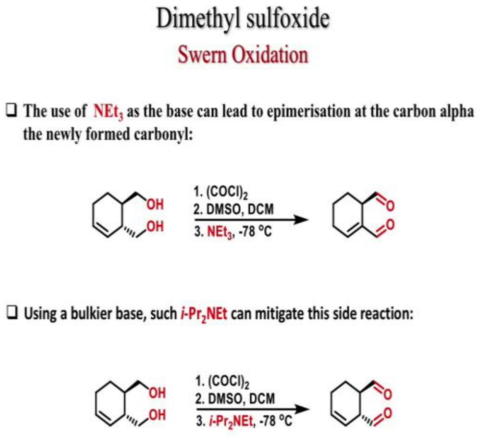

Dimethyl sulfoxide

Swern Oxidation

❑ The use of NEt_3 as the base can lead to epimerisation at the carbon alpha the newly formed carbonyl:

❑ Using a bulkier base, such $i\text{-}Pr_2NEt$ can mitigate this side reaction:

The use of triethylamine can sometimes, lead to epimerisation at carbon alpha to the newly formed carbonyl. So, this one is a; a double bond is here, and under Swern condition, it is found that the double bond moves to this position. And to, stop the epimerisation, it has been found that– if you use strong base, like, diisopropylethylamine, which is called Hünig base. And, under Hünig base condition, if you replace triethylamine with Hünig base, then you can stop this epimerisation and you can get this product selectively.

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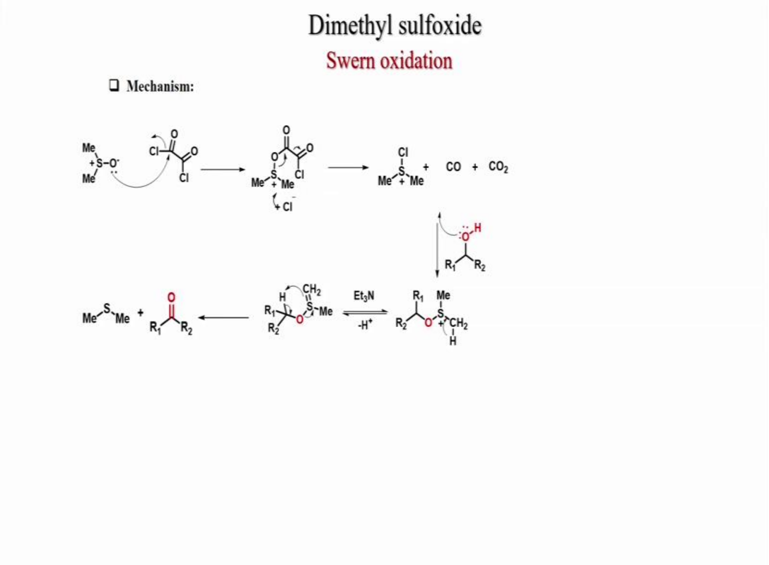

Dimethyl sulfoxide

Swern oxidation

❑ Mechanism:

So, what is the plausible mechanism of this reaction? Here, oxalyl chloride is an electrophilic species and DMSO can react here, and chloride minus will be as a leaving group, and you get this intermediate. And then, the chlorine minus, also is a nucleophile and it will react at the sulphur, atom and it will generate carbon monoxide, carbon dioxide, which liberates as gas. So, this process should be very facile, to generate this chlorosulphur complex.

Now, alcohol will react with this electrophilic sulphur complex, to generate this sulfenate salt. And, after treatment with diethylamine, we can think that, this proton might be more acidic, so this deprotonate first. And after this, helps to deprotonate this C-H proton and after that carbonyl compound will be formed and dimethyl suphide will be a byproduct.

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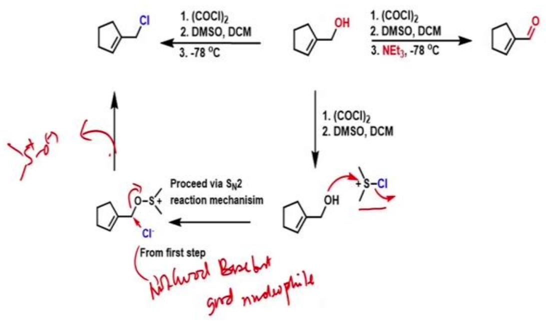
Dimethyl sulfoxide

Swern oxidation

- ☐ **Importance of Base:**



In Swern oxidation, importance of base; so, base is very important, in Swern oxidation. Suppose, if you use this allylic alcohol as the substrate, and in Swern oxidation condition oxalyl chloride, DMSO, dichloromethane, triethylamine, minus 78 degree centigrade, you get the alpha,beta unsaturated aldehyde. On the other hand, if you do not put triethylamine, the base, then what happen?

Then, under the similar condition, like oxalyl chloride, DMSO, DCM and minus 78 degree centigrade, you get the allylic chloride. So, what is happening? So when; we have already seen in the mechanism, that when you put oxalyl chloride and DMSO, you get this species, sulfenyl chloride. And, now the alcohol reacts with this sulfenyl chloride, to generate the sulfenium salt.

And now, in sulfenium salt, we know that chloride; chloride minus is not good base not good base, but good nucleophile. So, what will happen? The Cl minus is, if there is no treithylamine; now the Cl minus will not deprotonate this S, instead this will, it will do an S_N2 displacement reaction, and you get DMSO here. You get DMSO back and you get the allylic chloride. So, that is the importance of the base. So, without base, in Swern condition, you will not get the desired aldehyde; instead you will get the chloride.

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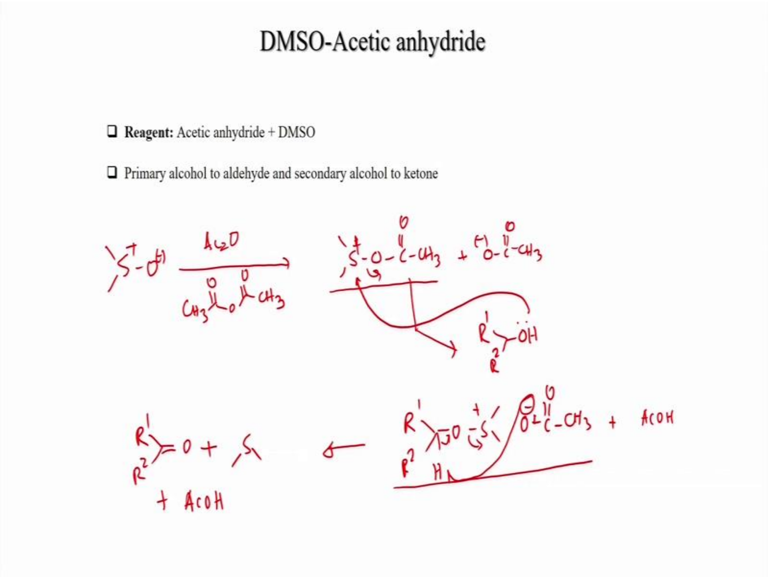

DMSO-Acetic anhydride

- ❑ **Reagent:** Acetic anhydride + DMSO
- ❑ Primary alcohol to aldehyde and secondary alcohol to ketone

So, DMSO Acetic anhydride is also an oxidation method. Here, acetic anhydride and DMSO is used and generally primary alcohol to aldehyde and secondary alcohol to ketone. And, in this procedure, you can see that external base is not used. So, what will be the mechanism of this reaction?

So, first DMSO reacts with acetic anhydride. If we write full also, it will be like this. And, now get; the activated DMSO is formed, plus $OCOCH_3$ negative. And now, alcohol, like R^1R^2 OH, it reacts and you get. So, this sulfenate salt is, generated and there one molecule of acetate anion and other molecule of acetic acid is generated.

Now, this acetate anion; this actetate anion is basic enough to do the deprotonation. So, you get the carbonyl compound plus dimethyl sulfide plus acetic acid. So, this is the overall reaction that acetic anhydride DMSO is also a good oxidizing reagent. And, under this condition, sulfoxide gets reacted with acetic anhydride to get this species and now, the alcohol can react; this is the activated anion. Now, the alcohol will react and generate this sulfenium salt, which on deprotonation by the acetate anion will generate the carbonyl compound and dimethyl sulphide and, acetic acid will be generated also.

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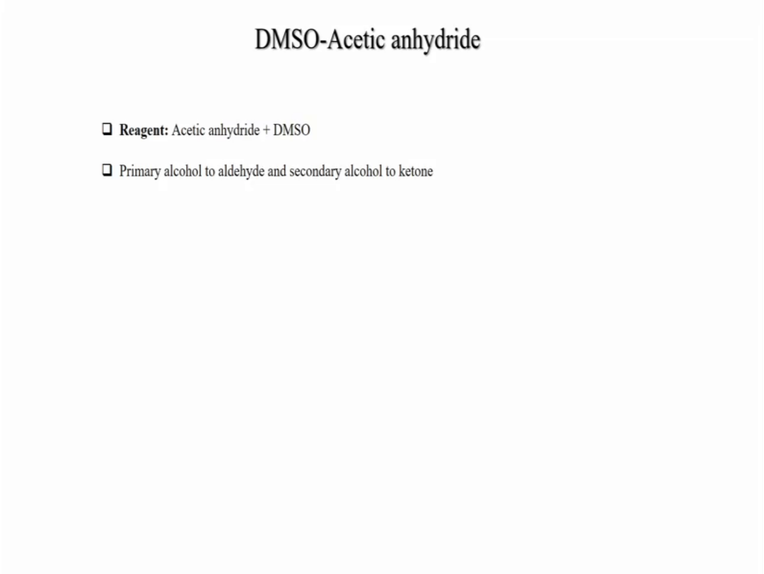

DMSO-Acetic anhydride

❑ **Reagent:** Acetic anhydride + DMSO

❑ Primary alcohol to aldehyde and secondary alcohol to ketone

DMSO Acetic anhydride is also has been used as a oxidizing agent. And this, here instead of trifluoroacetic anhydride, whatever we have seen earlier, here acetic anhydride and DMSO was used. And, this also primary alcohol to aldehyde and secondary alcohol to ketone.

So, in this lecture, today we have first discussed the Etard reaction, which does benzylmethyl group, like toluene compounds to benzaldehyde and then, we have seen DMSO based oxidations reaction. First we have see Kornblum oxidation, where alkyl bromide or tosyl reactant is used. Then, we have seen the Barton modification, where chloroformate was used. Then, we have seen the PfitznerMoffatt oxidation, where DCC and under phosphoric acid conditions, DMSO, DCC can give the product.

And, then we have seen in the Parikh condition SO_3 pyridine condition; SO_3 pyridine complex, which activate DMSO and triethylamine base. This condition is very mild condition and many natural products synthesis also, this oxidation has been used. Also, Corey Kim oxidation, which used the N-chlorosuccinimide as the electrophilic reagent and instead of DMSO, DMS is used. And, under this condition, this electrophilic species generated, which reacts with the alcohol to generate the aldehyde.

Then, we have seen the Swern oxidation. Earlier Swern oxidation was with trifluoroacetic anhydride. And, later Swern developed; the modified version, which is well-known as Swern oxidation, where oxalyl chloride is used. And, oxalyl choride, first reacts with the DMSO, and; to generate an intermediate, which after carbon monoxide, carbon dioxide elimination, generates the chlorosulphur complex. The, alcohol reacts to generate the sulfenate salt. And, after triethylamine reaction, you get the aldehyde or carbonyl compound. Thank you.