

Molecular Rearrangements and Reactive Intermediates in Organic Synthesis

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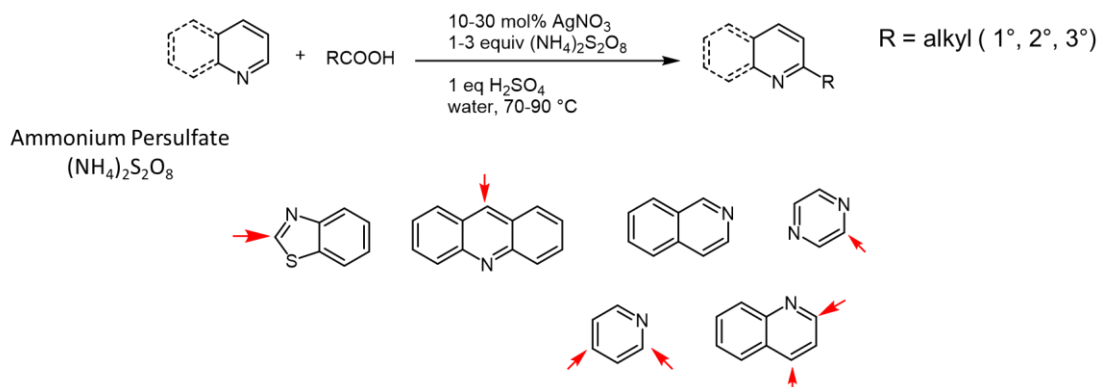
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Lecture 19: free Radical

Welcome back to this NPTEL online certification course in the molecular rearrangement and reactive intermediates. In the last class I talked about the decomposition reaction and generation of free radical. If you remember I was talking about the Barton decomposition reaction, I was talking about the Hunsdiecker reaction. In the today's class we are going to talk about the generation of free radical then decomposition reaction and then how to add them to the heteroaryne. So, I am going to start with this very important Minisci reaction which I could not cover in the last class. And after covering the Minisci reaction I am going to introduce you is the organic photochemistry of carbonyl compound and from there I am going to talk about the Norrish type 1 and Norrish type 2 cleavage.

So, let us start about the Minisci reaction. It was discovered in 1971 by Professor F. Minisci. What is happening here? It is actually generation of a radical from the carboxylic acid in the presence of silver nitrate and ammonium persulfate in presence of H_2SO_4 .

The substitution of protonated heteroaromatic bases by nucleophilic carbon-centered radicals is known as the **Minisci reaction**, The reaction was published in 1971 by F. Minisci

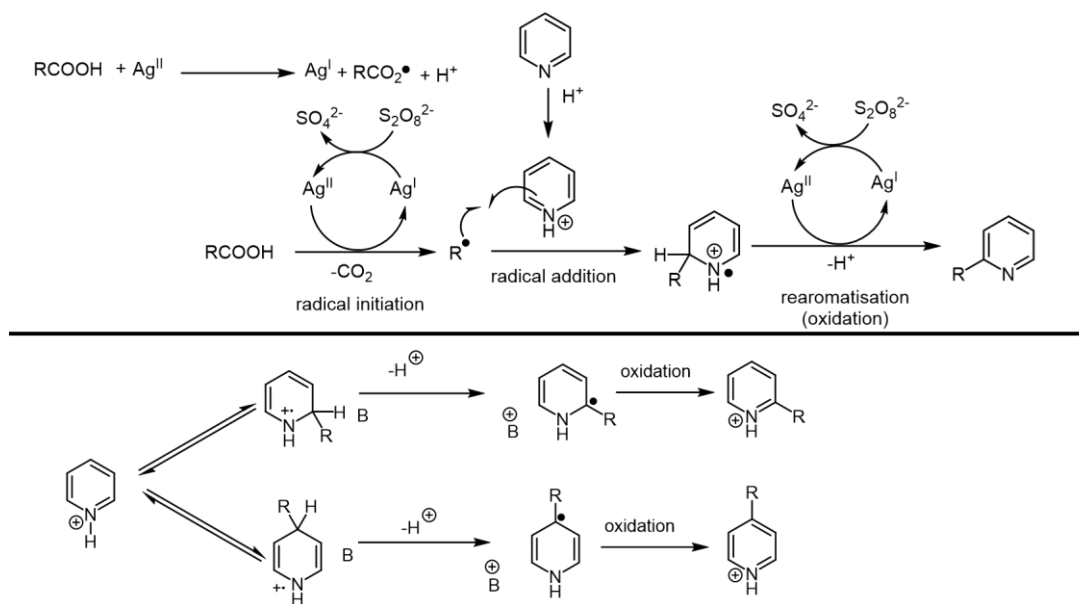


So, the H_2SO_4 actually making this as a protonation happening here and then the silver nitrate and ammonium persulfate actually the silver nitrate is playing important role to generate the radical here which is going to add to this type of heteroaryls to get to the

alkyl heteroaryl product. So, it could be alkyl or aryl based on the radical you generate. Now once it will form it can add to the position where the corresponding intermediate after addition of this radical species the where the intermediate going to get stabilized those are the position where it is going to add. You can see these are the electron deficient position for the corresponding heteroaryl. So, if you see for the corresponding quinoline this is the position where it is going to add.

If you have a pyridine, we know that the nucleophile going to attack in this C-2 and the C-4 position. here if you have a quinoline also you can see there is a C-2 and the C-4 position where the radical can attack. So, here I think one of the important things is the radical you are generating are mostly nucleophilic. So, now what is going to happen now it is need to be protonated. So, that now it is going to become an electrophilic species.

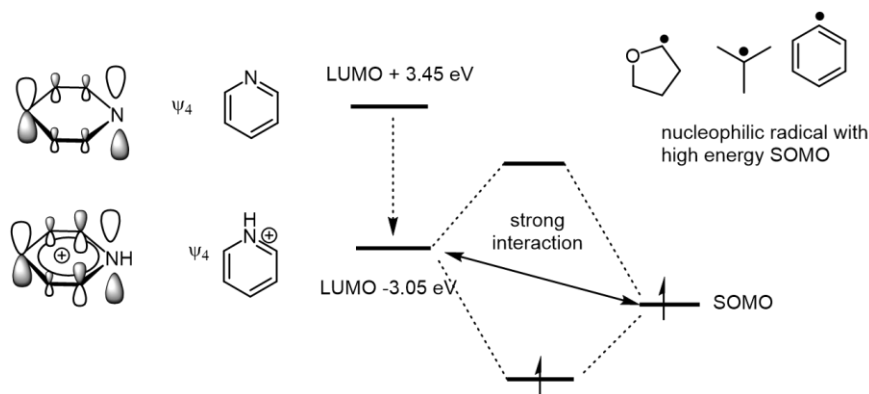
So, that radical can comfortably add here. So, before you try to understand the mechanism the important things to remember in this reaction that silver, we are using in catalytic quantity. And we are using ammonium persulfate in stoichiometric quantity. The Ag(I) is actually initially getting converted to Ag(II) here. Now, what is going to happen this Ag(II) going to take a single electron from this carboxylate anion.



So, now, once it will take one electron the Ag(II) going to convert a Ag(I) and this is going to convert to the carboxyl radical. And once you are forming it is going to participate in decarboxylation reaction to form this corresponding radical. Now, once this is formation happening this is the radical initiation step. Now, the next thing is the radical

addition happening. So, the radical is now going to add to this the corresponding the it can add to this C 2 position here or it can add to this corresponding C 4 position here.

So, after the addition happens there will be a proton abstraction is happening. After the addition is happening here there will be a proton abstraction and then there will be a re-aromatization. So, what is going to happen this species is going to get oxidized to the corresponding product. After the proton abstraction what is going to happen you can see the from the from the nitrogen one electron will be taken by this ammonium persulfate to finally, reoxidize it to the corresponding the alkylhetero aromatic compound. Again, I know as I mentioned that why this reaction happening here, we have this list of this nucleophilic radical to interact with the corresponding pyridine it has to form this corresponding pyridinium. That means, the the acid has a very key role here to convert this pyridine to the pyridinium. So, that now the LUMO can come down here. So, that this single occupied molecular orbital can interact with the LUMO. So, this interaction is only possible once this pyridine is getting protonated to the corresponding pyridinium.

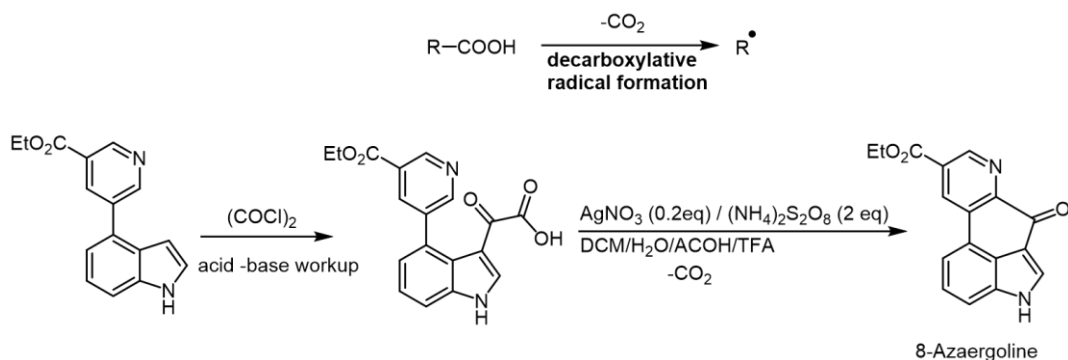


Explains higher reactivity of cationic form due to lower LUMO

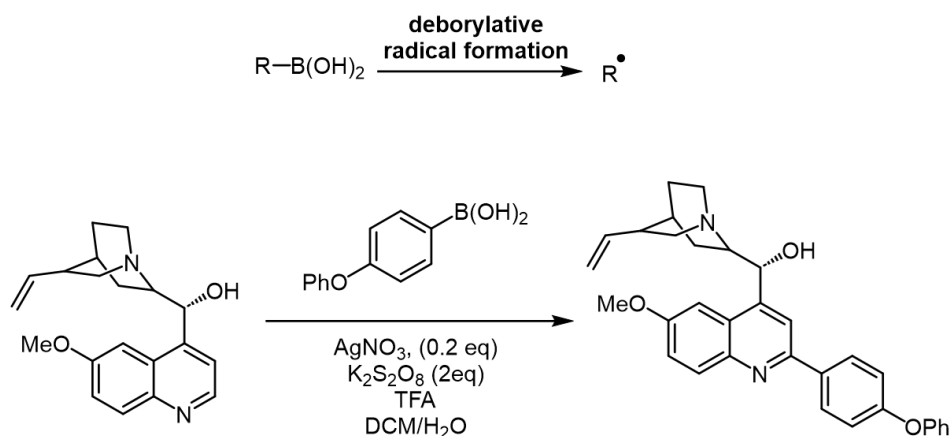
- ❖ Correctly predicts preferential reactivity at 2- and 4-positions of pyridinium ion

First of all, so this reaction after the initial discovery this reaction become little more general and there is different method was developed how to generate radicals. First thing we have learnt from the carboxylic acid it can generate this radical.

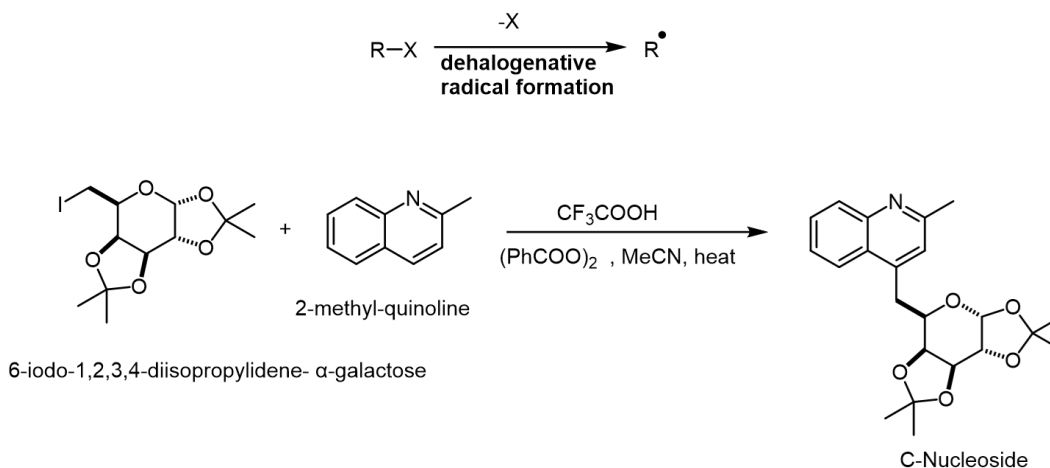
In this reaction first step using the oxalyl chloride it is introducing this electrophilic group in the C-3 position here this α -hydroxycarboxylic acid finally, in presence of silver nitrate generating the corresponding the α -acyl radical which is going to add to this in heteroaryl in the C-2 position here to form this corresponding product.



As I mentioned the radical can be formed from the corresponding boronic acid using the silver nitrate and again very similar type of reagent which was used for the Minisci reaction to generate the radical species here they are generating aryl radical which can add to this corresponding C-2 position to get to this product. Again, in here the C-4 position is blocked, so it is attacking in the C-2 position.

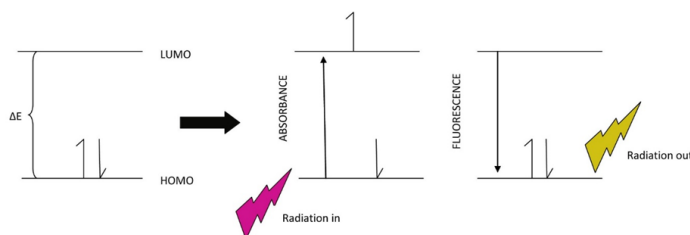


Another example, here the radical is generating from corresponding alkyl halide. So, here you have to use this corresponding benzoyl peroxide. I have already mentioned that from benzoyl peroxide you can able to in presence of heat it can cleave this O-O bond to generate a radical species. which can able to cleave this C-I bond to generate a radical which is now going to add. So, now it is going to get protonated and the radical is going to add selectively to the C-4 position to form this corresponding nucleoside here.

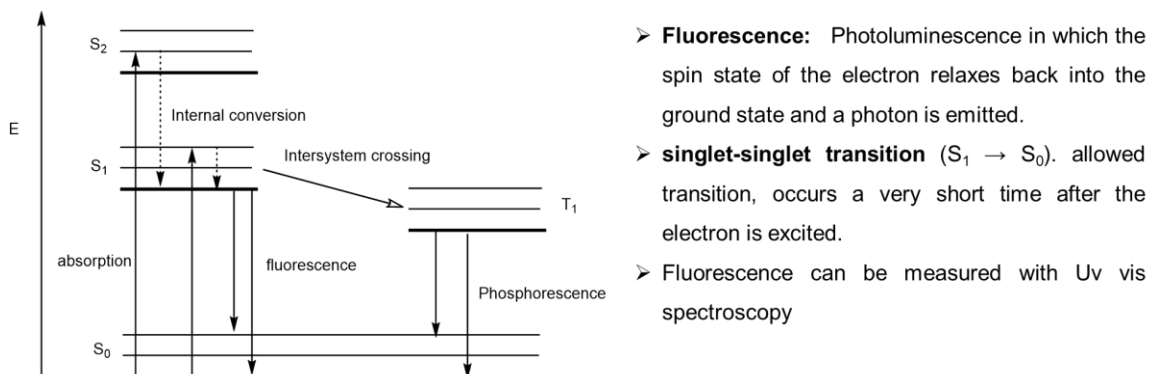


So, in the first part I talked about the Minisci reaction and now I am going to move to the photochemistry of the carbonyl compound. So, before you try to understand the photochemistry, we have already learned the Planck equation. That means if you shine light or if you put UV light into a compound or a molecule which can absorb the light and once it absorbs the light, it will get excited, and once it is excited, it is going to move from the corresponding HOMO to the corresponding LUMO. After it absorbs the energy, so once you give $h\nu$, it is going to actually move from the corresponding HOMO to the LUMO. Different type of molecule has different type of energy level. So, if you have a σ -bonding then it could be a σ to σ^* . So, that could be your HOMO LUMO, if you have a π then there could be a π to π^* transition. So, that will be a HOMO LUMO. So, that can happen and if you have a nonbonding electron then it could be a n to π^* . So, depending on the different bonding present in the molecule and what is the absorption happening if it is happening in the how much energy it is getting. Based on that this type of transition going to happen from the HOMO to LUMO.

When a molecule absorbs a photon of a particular wavelength, the molecule is raised to a ground electronic state to a higher electronic states depending on the amount of energy provided by the photon. Electronic transitions involve exciting an electron from one principle quantum state to another



So, I was trying to explain through this Jablonski diagram. It is a very important diagram. It illustrates or it actually it demonstrates the excited state molecule along with the the relative non-radiative and the radiative transition.



a diagram that illustrates demonstrates the excited states of a molecule along with the radiative and non-radiative transitions that can occur between them

First from the from the S_0 once it is getting energy it can go to the S_2 which is the the higher excited state singlet orbital from there through a non-radiative process internal conversion it can come down to S_1 . from S_1 it can go for a fluorescence to release the energy or it can go for intersystem crossing (ISC) to convert from singlet to the corresponding excited triplet. From the excited triplet it can come back as a phosphorescence. So, I already mentioned here the in the fluorescence process the photoluminescence is the spin set of electrons relax back to the ground state and there will be photon is going to be emitted. And I also mentioned about the phosphorescence. And you can see that the singlet to singlet transitions are allowed and the singlet to triplet transitions are forbidden.

So, I am going to discuss them here. So, you can see I already talk about the internal conversion which will be a non-radiative transition. So, here you can see it happen from this S_2 to S_1 and there will be no photon is getting emitted. And the electron spin state also the remain same.

Internal conversion

- non-radiative emission,
- electron moves from a higher energy excited state to a lower energy excited state. (S_2-S_1)
- This occurs when the vibrational modes of different electronic levels overlap.
- No photon is emitted
- **electrons spin state remains the same**

Phosphorescence

- type of fluorescence
- electron relaxes into the ground state via emission of a photon
- **T_1-S_0 transition.**
- This is a forbidden transition, so happens over a much longer time scale.
- **measured with UV-Vis spectroscopy**

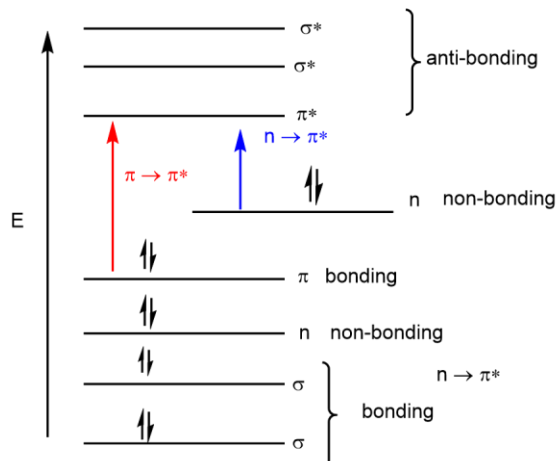
Intersystem crossing

- non-radiative emission
- the **spin state of the excited electron changes.**
- **S_1-T_1 transition**
- results in phosphorescence emission

I also talk about phosphorescence it will be T_1 to S_0 transition going to happen and this is the forbidden transition as I mentioned. And then I also mention about the inter system crossing. So, here the spin state of the excited electrons changes and this is a S_1 to T_1 transition.

So, now I am going to talk about specifically about the carbonyl as I mentioned that we are going to focus on the carbonyl chemistry. Now if I try to draw a carbonyl compound a general. So, what are the different bond it has it has a σ bond that means, there will be a σ you can see there are two σ bond here. So, these are the bonding orbitals if a bonding orbital, then there will be must be there will be anti-bonding orbital means there will be a σ^* orbital and then if you can clearly see that there is a π -bond here we can draw them here.

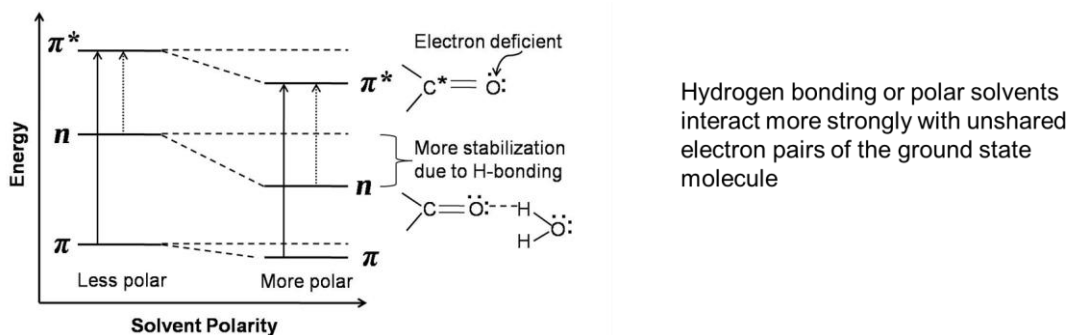
carbonyl transition



Compound	$\lambda_{\max} \pi \rightarrow \pi^*$	$\lambda_{\max} n \rightarrow \pi^*$
Cyclohexanone	200 nm (ϵ 2000)	285 nm (ϵ 14)
$(CH_3)_2C=CHCOCH_3$	230 nm (ϵ 12,300)	325 nm (ϵ 90)
C_6H_5CHO	242 nm (ϵ 14,000)	328 nm (ϵ 50)
$C_6H_5COCH_3$	238 nm (ϵ 13,000)	320 nm (ϵ 40)

So, if there is a π -bond then we can always say that. So, there will be a π^* orbital I can draw the π^* here. So, this could be the π^* orbital and at the same time if you have a oxygen here then you have to also understand that the oxygen will have a non-bonding orbital. So, oxygen will have a non-bonding orbital. Now, you can see that. So, whatever transition can happen we will we have learned there is a π -bonding then there is a non-bonding. So, now, this it can happen that it can σ to σ^* or the π to π^* and n to π^* you can clearly see from the diagram that there is a n to π^* transition can happen or there is a π to π^* transition can happen once we excite with the light. There is a difference between the energy level if you see different type of ketones I am going to discuss in further, there will be difference in the energy you need to go from π to π^* or n to π^* . So, what we are mostly interested that once you shine light to the carbonyl compound there will be the n to π^* transition, where we are going to talk about some chemistry.

So, another important thing of this type of photochemistry is solvent. So, solvent polarity also plays very important role here because for carbonyl compound once you have a polar solvent like ethanol then the hydrogen bonding with this carbonyl compound is going to stabilize your non-bonding ground state even more than the corresponding excited state. So, what is going to happen if it is stabilized more, then you need actually more energy to go to this n to π^* in case of a polar solvent. So, that does not happen in case of the π^* orbital. So, there are actually several factor for this type of photochemical reaction one of them is the solvent polarity.



The other important thing is the carbonyl selection rule. So, as I was trying to mention you from the structure let us go to the structure again. So, what I was trying to talk about. So, there is this π^* . So, this is a π^* orbital and you have this. So, now this π^* orbital is actually perpendicular to the carbonyl group.

Generally, you can think about the carbonyl group actually in the plane and also the carbonyl non-bonding orbital actually in the plane. the carbonyl oxygen non-bonding. So, these are actually also in the plane of the carbonyl, but these π^* orbital actually in the

perpendicular to the plane. So, what is going to happen if I talk about a $n \rightarrow \pi^*$ transition, there is a problem happening because if you think about this is a π^* and this is a n , non-bonding electron then $\pi \rightarrow \pi^*$ transition is getting difficult. So, once you try to understand the selection rule it is saying orbital overlap in space is the problem.

Carbonyl selection rule

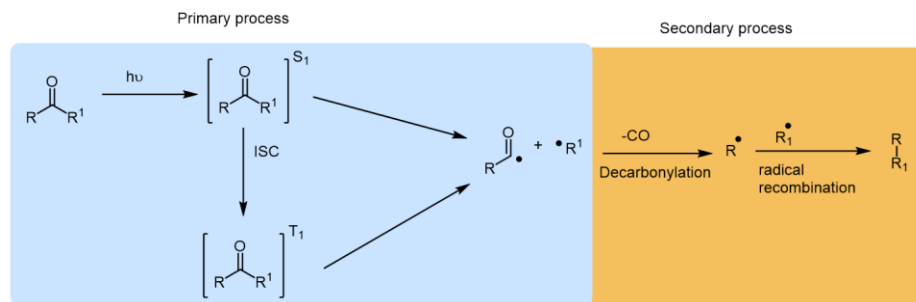
Transition	Probability	Factor
$S_0 \rightarrow S_1(n, \pi^*)$	Forbidden	orbital overlap in space (also symmetry)
$S_0 \rightarrow S_1(\pi, \pi^*)$	allowed	
$S_n \rightarrow S_1 \rightarrow S_0$ $T_n \rightarrow T_1$	allowed	no change in spin multiplicity
$S(n, \pi^*) \rightarrow T(n, \pi^*)$ $S(\pi, \pi^*) \rightarrow T(\pi, \pi^*)$	forbidden	change in spin multiplicity
$S(n, \pi^*) \rightarrow T(\pi, \pi^*)$ $S(\pi, \pi^*) \rightarrow T(n, \pi^*)$	forbidden	change in orbital configuration

Since NBMO and antibonding π^* MO are perpendicular to each other, the $n \rightarrow \pi^*$ transition in the carbonyl compound is overlap forbidden. However, due to unsymmetrical molecular vibrations, this transition takes place slowly.

So, that is why this is a slow transition. So, the non-bonding molecular orbital and antibonding π^* orbitals are perpendicular to each other that is why $n \rightarrow \pi^*$ transition in carbonyl compound is overlap forbidden. However, it takes place very slowly. So, this is one of the important things here and then the other things here now if you talk about from S_1 to S_0 or T_n to T_1 that means if you are converting from a singlet to a singlet or triplet to triplet are allowed, but once you from singlet to triplet or here you can see from $S(n, \pi^*)$ to $T(n, \pi^*)$ or here also $S(\pi, \pi^*)$ to the $T(n, \pi^*)$ that means, from singlet to triplet what is actually they are forbidden. So, there is a change in spin multiplicity going to happen.

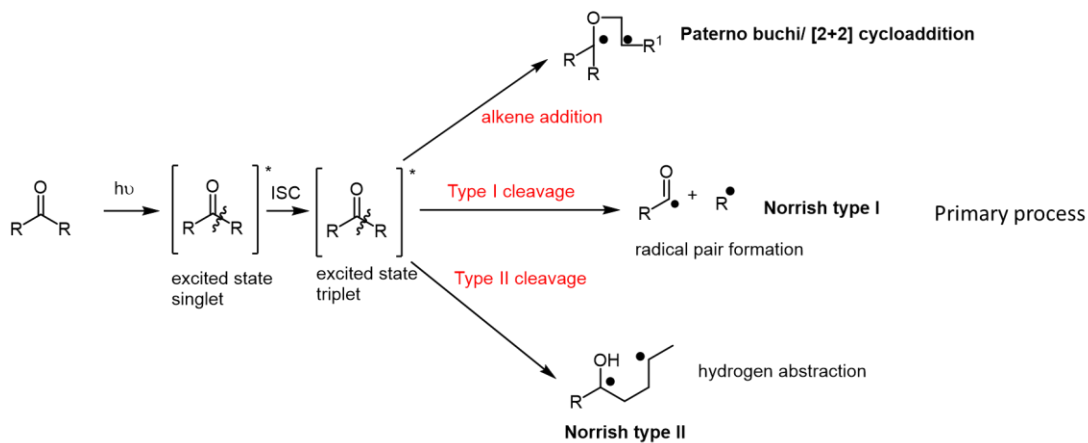
So, we have learned that once you shine light to the carbonyl compound. So, generally we can write this way that if you have a reactant here and you shine light then you first make the excited state species it could be excited state singlet if you write singlet here then it going to go for an intersystem crossing as I mentioned to go to excited triplet and from there it will form a intermediate and then it will form the product. So, now once you shine light to the corresponding carbonyl compound what is going to happen? First you will have seen that the $n \pi^*$ one which is going to the dominate this chemistry of the carbonyl compound. So, most of this chemistry of carbonyl compound actually dominated by this $n \rightarrow \pi^*$ transition. Of course, there are some chemistries by benzophenone which is dominated by the π, π^* , but the majority you will see with the n, π^* .

The Norrish type I reaction is the photochemical cleavage or homolysis of aldehydes and ketones into two free radical intermediates (α -scission).



So, what is happening here first thing is as I mention here once you have this carbonyl compound first thing it is going to get to this corresponding singlet excited singlet intersystem crossing excited triplet. So, mostly from the triplet you will go to see that the first thing is going to happen is the α -scission going to happen. So, once it is going for the α -scission to generate this acyl radical and this radical we call this radical pair. So, this radical pair formation happens. So, up to this is actually a primary process. After that the secondary process starts. What is going to happen in the secondary process? It is going for a decarbonylation to generate a $R\cdot$ and then there could be a radical recombination happen to form this $R-R_1$, but you will see in the real example there could be a hydrogen abstraction also going to happen.

So, now I am going to talk about the different possibilities here. So, first thing I mention that once you shine light under UV it is going to the excited state singlet then intersystem crossing to excited state triplet. Then you can see the first thing I mention about this the formation of this α -acyl radical to the type I cleavage α -acyl. It can go for a type II cleavage if you have a corresponding β -hydrogen sorry if you have corresponding γ -hydrogen.

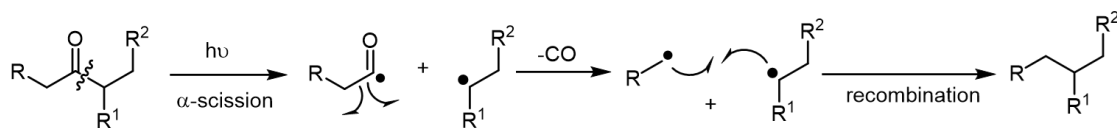


The Norrish Type I process is mostly favored by photolysis in the vapor phase and is less pronounced for photolysis in the inert solvents

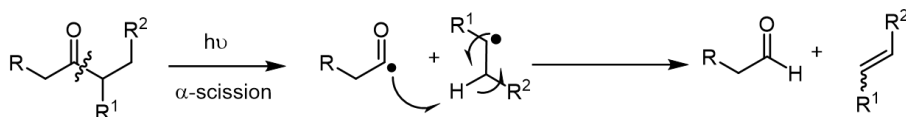
So, if you have corresponding γ -hydrogen you can see here it can go for a hydrogen abstraction I am going to explain you why this is favorable. So, that is a Norrish type II cleavage to generate this type of diradical species one for diradical species which can have a several fate. I am going to explain them. And then the other thing is once this type of radical species forming that means from here once you are generating in the excited triplet state the next is going to happen So, once you are generating this species it can also going to add to a corresponding olefin. So, that is going to bring to this in a reaction, called Paterno buchi reaction. So, that means, this species can add to an olefin and it can also go for a type I cleavage means in the α -session going to happen or it can go for a type II cleavage which is the γ -hydrogen.

So, once you are going for this abstraction as I mentioned the first thing sorry once you going for the cleavage to generate the acyl radical, it can generate alkyl radical after the decarbonylation, then there is a recombination to get to this product. As I mentioned that it can also able to go for a hydrogen atom abstraction here. So, this R' can able to go for a hydrogen atom abstraction. to generate a radical species from there it can able to form this cis and trans and then the corresponding aldehyde or it can go for a ketene formation. That means, first it will generate this corresponding acyl radical So, it will go for this radical pair and then it is going to.

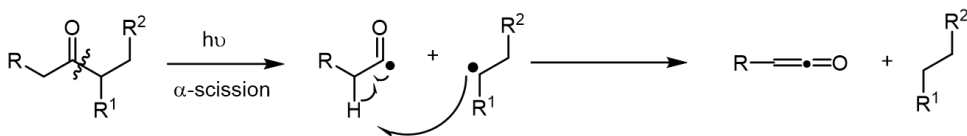
Radical recombination



H-atom abstraction



Ketene formation



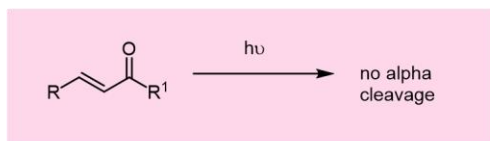
So, this radical going to go for a hydrogen abstraction here. to generate a radical species here which can form the corresponding ketene and then it will form the corresponding alkane.

So, couple of important things that once this type of cleavage is happening that suppose you have a carbonyl group here one side you have a tert-butyl group one side you have a methyl. Then once the cleavage is happening it is going to form the more stable radical pair that means, if you see about this one versus if I suppose I think here the R will be methyl. Now, versus if you have created this one, then you can see here it is forming the more stable radical that is why this will be favorable. And after the formation of that it has multiple fate it can go for a dimerization, it can go for a hydrogen atom abstraction to form in a different set of compounds is another thing here of course, here also it can go for cleaving it to generate this corresponding radical, once you have this radical again as I mentioned it can go for a dimerization, it can go for a hydrogen atom abstraction. Now, the question comes every time I am talking about the radical cleavage and generation of a radical which are alkyl group. Now, sp^3 hybridization what about if you have a sp^2 scenario that means, if you cleave where you have a sp^2 or sp that means, if you have generated a vinyl radical is that a possibility? No, I think the generational vinyl radical will be difficult, because you can see once you form this radical it will be unstable.

❖ Reaction proceeds to form more stable free radical

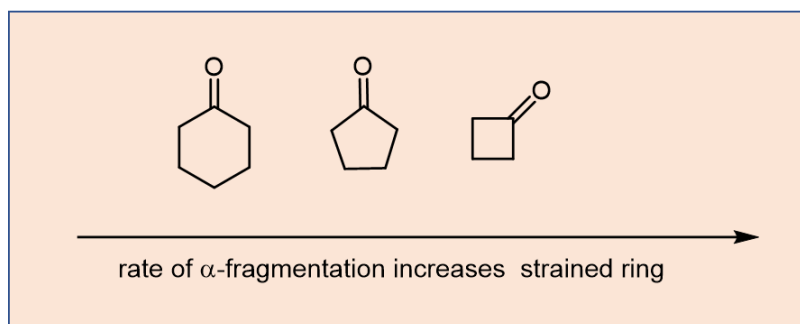
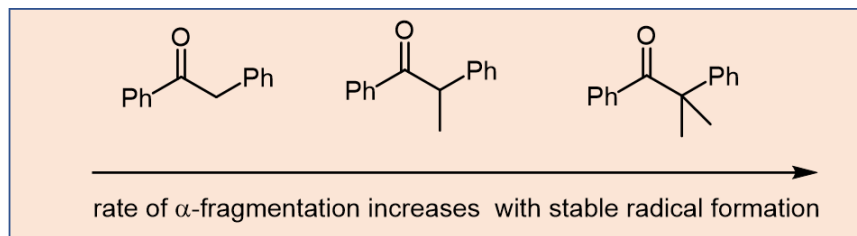


❖ The sp^2 and sp nature of α - carbon never participated in Norrish type I

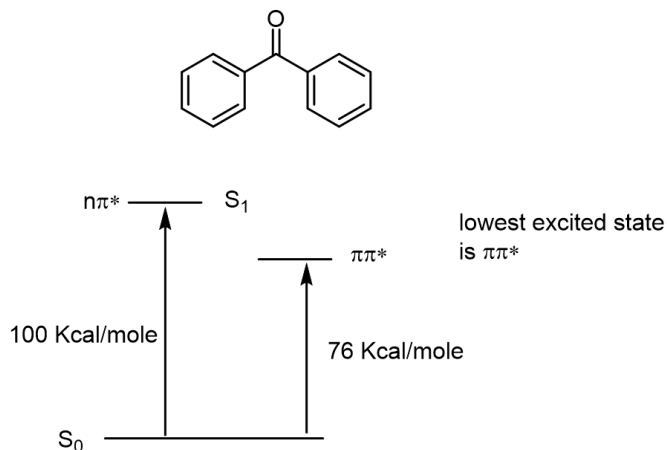


So, the factors affecting the Norrish type I, I think the rate of α -fragmentation increases with the stable radical formation. As I was telling you that once you go for this α -scission you are generating this corresponding radical, now the radical stability is the guiding factor and it is actually controlling the rate of the α -fragmentation. And again, if you have a strain in the molecule that if you have this cyclohexanone, cyclopentanone and the

cyclobutanone you are increasing the ring strain. So, that is actually once you have the high ring strain it will try to open up.



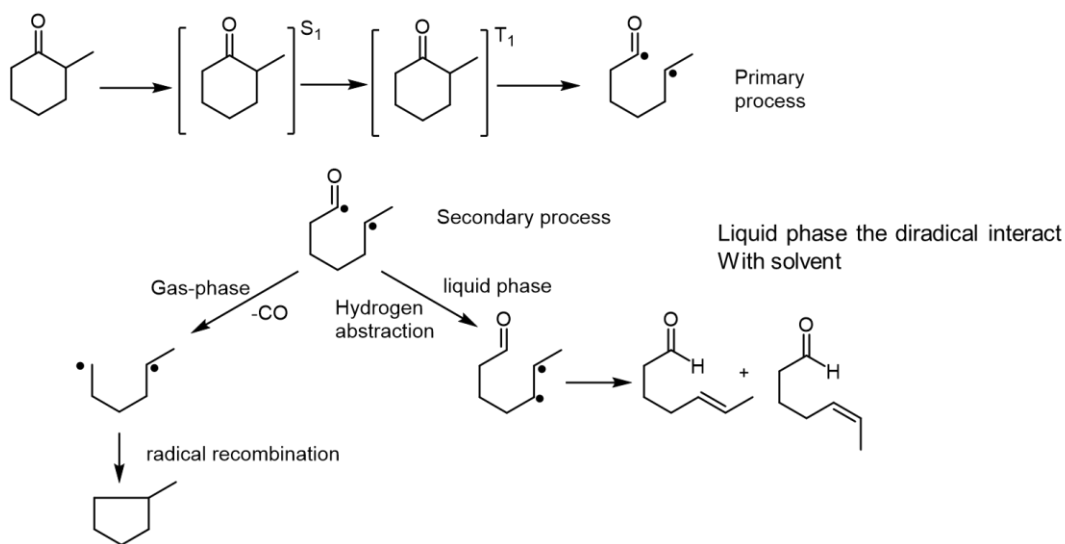
The other important is that the benzophenone actually does not participate in the Norrish type I. So, not only just by looking into the benzophenone you might say sir if I am going to cleave it, I am going to generate this phenyl radical that is not only the reason for that. The other important thing is if you see about the photochemical process, it always happens through the lowest energy excited state.



Photochemistry happens from the lowest excited state so no Norrish I cleavage
Benzophenone is used a photosensitizer for that reason

So, here what is going to happen if you see about the n to π^* it is almost 100 kcal/mole, but here if you see about the π to π^* then you can see it is 76 kcal/mole that means, the lowest excited state is π to π^* not the n to π^* . So, that is why you can see lot of the π to π^* chemistry going to happen we using this you can use as a photosensitizer, but not for the Norrish type I.

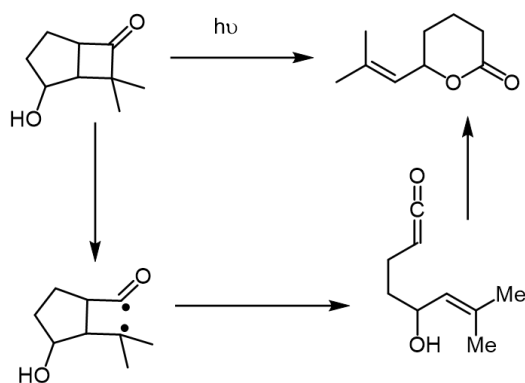
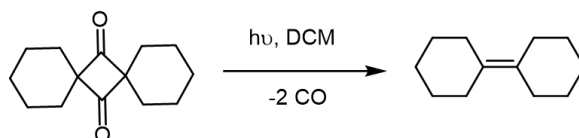
So, now another important thing about the vapor phase and liquid phase. So, first I think if you start from this compound, I am going to show you what will be the different product again, after you give the $h\nu$ it will go to the corresponding singlet excited state from the intersystem crossing it will go to the corresponding triplet excited state from there it is going to form this type of.



So, it is going to go for α -scission going to happen to generate this radical pair which is a primary process now that the next thing is what is going to happen after this. So, you can see the in case of gas phase there is a decarbonylation going to happen which is going to generate this radical pair. So, now, it can go for a radical recombination that means, in the gas phase what is happening the decarbonylation reaction is happening, then in the liquid phase what is happening there is a hydrogen abstraction that means, this radical now can able to abstract hydrogen to form a radical. So, that way it is going to form this species and now what is going to happen that as you can see there are two radical species it can go either from forming this as a major and this as a that the cis as a minor. But the question is what is happening here in the gas phase also. So, in the liquid phase it can interact with the solvent in the gas phase that is difficult. So, the reaction is. So, reaction happen also with some temperature. So, that is why the decarbonylation happen in the gas phase, but in the liquid phase it is going for the hydrogen abstraction because interact

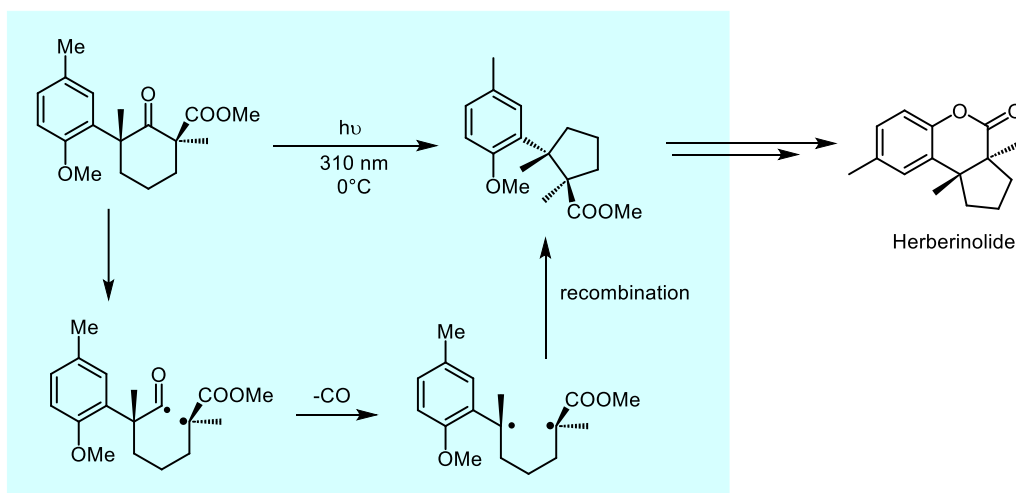
with the liquid. So, it is tried to stabilize with the radical and go for a hydrogen abstraction instead of the decarbonylation.

Some of the application here this is a very interesting example you can see two carbonyl group here it is a cyclobutanone with two carbonyl group first thing is happening first there is a α -cleavage to generate a radical here then there will be CO going to eliminate to generate a radical so first there will be radical to form a bond there will be α -scission here generate a radical and then with the again there will be carbon monoxide going to eliminate to generate another radical. So, you can see that is going to end up forming the double bond here, first single bond and then double bond.



There is another interesting example here as I mentioned if you have a cyclobutanone or type of things then it is first going to open up to form this type of radical pair And then in the gas phase I think I mentioned that the next thing can happen there is a cyclopentane ring which going to also going to open up to generate this type of as I mentioned you generate this ketene where this alcohol was present which going to cyclize to form this compound.

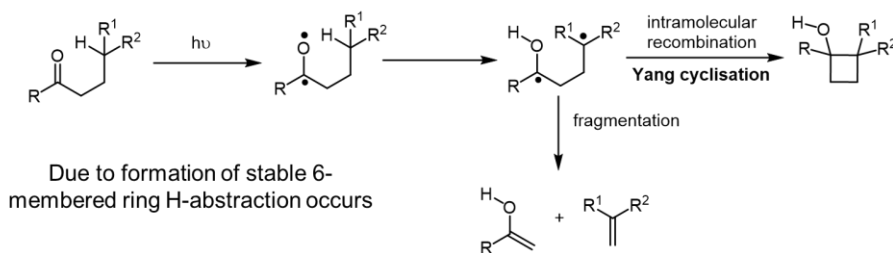
The other important example here what is going to happen in this compound for once you give $h\nu$ first thing is formation of the α -cleavage happening here why it is happening here why not the other side? You can see here you have this ester group here which is actually stabilizing this radical. Then the next thing will be in the gaseous phase there will be this carbon monoxide going to get out. So, there will be a decarbonylation to form this the more stable radical here. Once you have these two stable radicals, they can go for this recombination to form this compound. again, as this is forming a close radical pair here that is why you can see their stereochemistry will be the diastereoselectivity will be higher here which is going to convert to finally to this natural product.



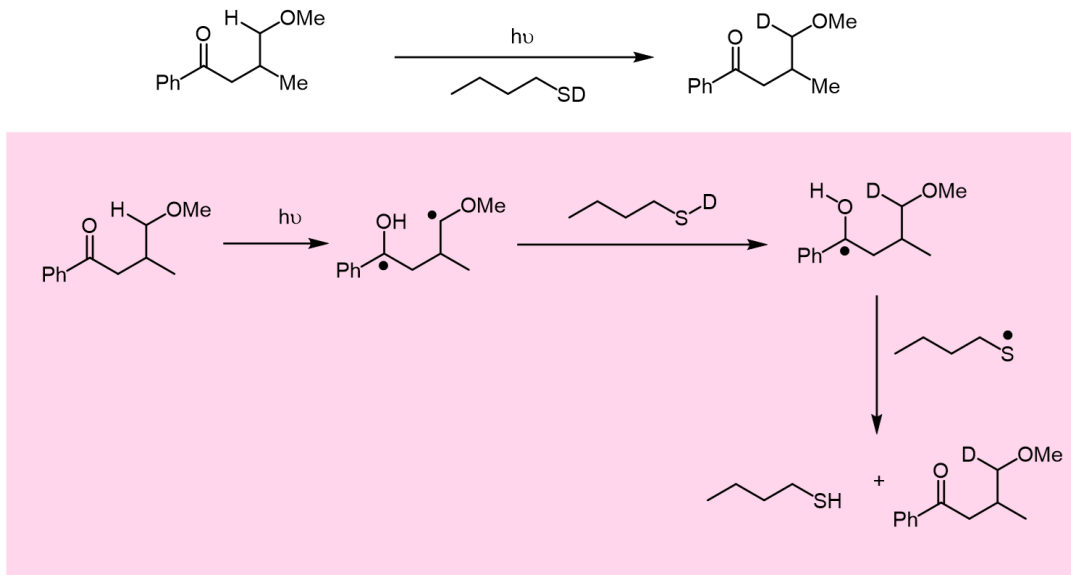
I am going to move to the Norrish type II, I have already mentioned at the beginning that once you have this carbonyl going to excite to the $n \rightarrow \pi^*$. So, once it is going to the $n \pi^*$ singlet or the $n \pi^*$ triplet, then the next thing is it can also go for the abstraction of the γ -hydrogen it is going go for the abstraction of γ -hydrogen through some sort of a six member type of a transition state which can abstract this γ -hydrogen to generate this type of 1,4 diradical species so it form a stable six member transition state as I mentioned so then what is going to happen from this one four 1,4 diradical species it can go for a fragmentation means this bond getting can cleave to make a radical and a radical here to form this type of enol and this olefin or it can go for a Yang cyclization where this two radical go for a radical combination to form this type of cyclobutane ring. Again, I think the ketone which have a low lying $\pi \pi^*$ state you do not undergo this reaction as I mentioned. So, that means again this is happening from the $n \pi^*$. So, as I mentioned before if your $\pi \pi^*$ is the lowest then it will not be going to happen.

A **Norrish type II** reaction is the photochemical intramolecular abstraction of a γ -hydrogen (a hydrogen atom three carbon positions removed from the carbonyl group) by the excited carbonyl compound to produce a 1,4-biradical as a primary photoproduct.

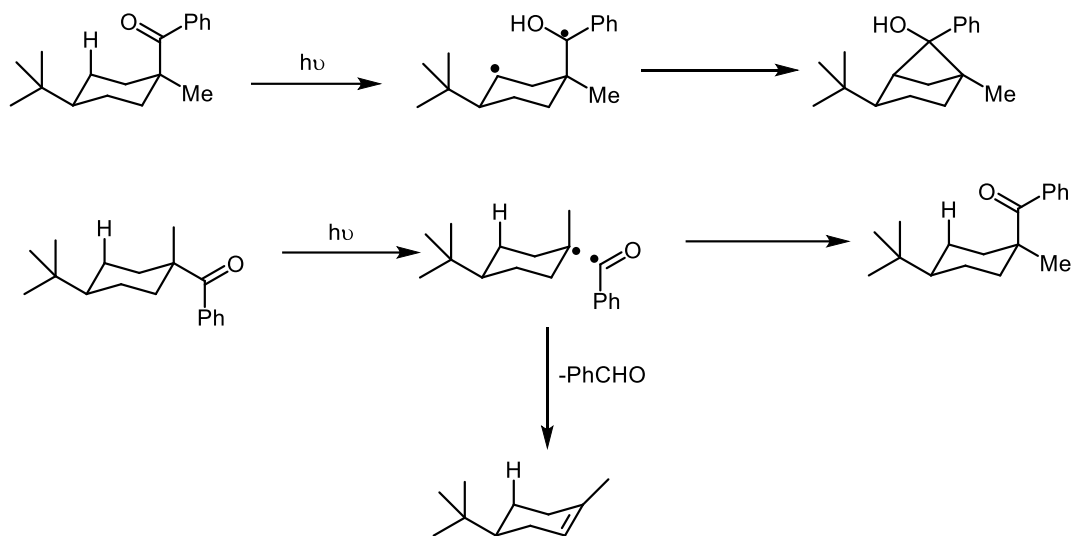
Both n, π^* singlet and n, π^* triplet participate in the intramolecular hydrogen abstraction reactions while [ketones with a low lying \$\pi, \pi^*\$ state do not undergo this reaction.](#)



Here there is an important example here for starting from this once you give $h\nu$ it is going to first it is going to go for this hydrogen abstraction. And then what is happening you have this compound here that the S-D which is going to cleave this bond to take this deuterium here and now this H' can able to go for hydrogen atom abstraction to form this O' which is going to finally form this product. So, that is how this deuterium is getting transferred here.

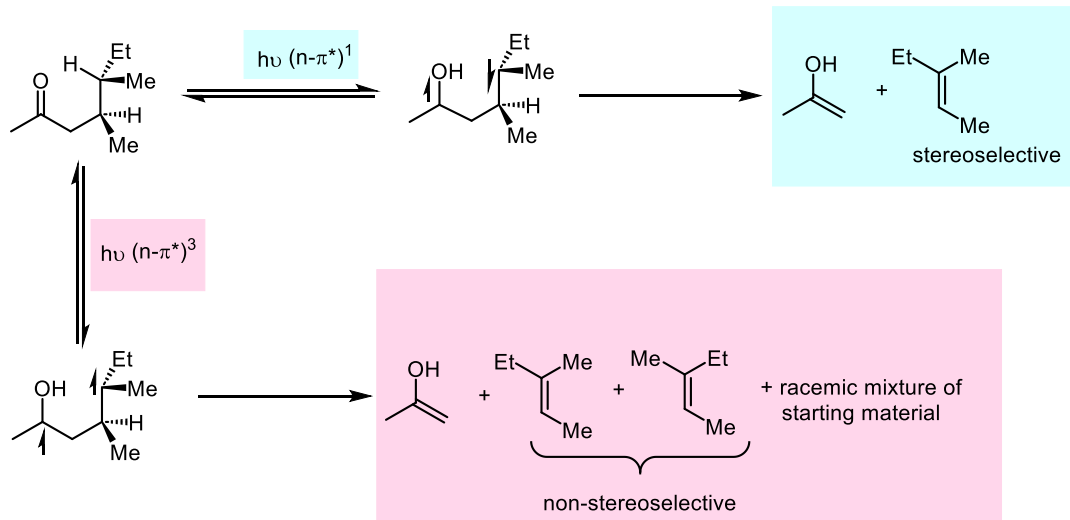


There is another important example where what I am showing here if you have a tert-butyl group then it always prefers the equatorial position. That means it is actually you lock the cyclohexane confirmation. So, now we can see you have a COPh group here in the axial methyl in the equatorial or you have a methyl axial COPh equatorial. Now what is happening? Once you shine light the in place of the UV light what is going to happen here? You generate this intermediate species after this the hydrogen abstraction. So, what is going to happen after that it can now go for this Yang cyclization to form this compound. But once you have this COPh is actually the not the same side of this hydrogen, what is happening here it can also go for a cleavage here to generate a stable radical here. As I mentioned if I have a stable radical it can go for a hydrogen atom abstraction to form this compound.

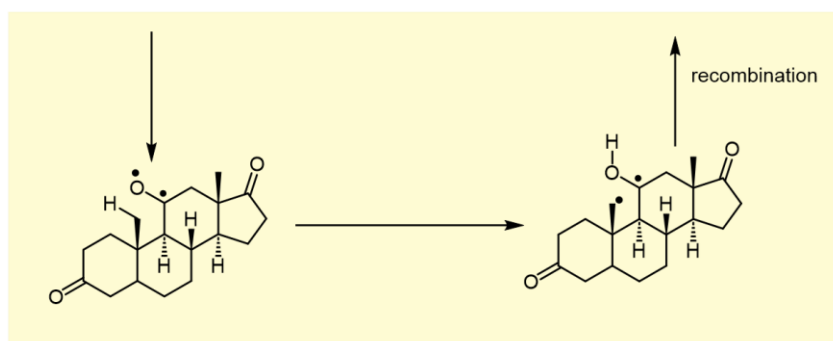
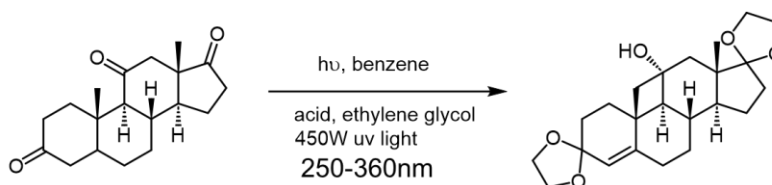


Another interesting fact about the Norrish type II, as I mentioned that it can happen from the $n \pi^*$ singlet or the $n \pi^*$ triplet. Now, the thing happens starting from this if it is happening from the singlet versus the triplet, we are ending up the product at the end where we are synthesizing some olefin one case, they are stereoselective once is going from the singlet and one case you are getting in the non-stereoselective mixture one is going from the triplet. So, let us try to understand what is happening first thing is that n to π^* first it is going to go to the excited states, then it is going to go for this hydrogen atom abstraction to form this diradical species. As you can see, they are singlet species here, the next thing is once the fragmentation is happening that means this bond is getting fragmented. So, let us have a closer look what is happening. If you remember once you are forming a bond then you can write them like this that they are in the opposite spin.

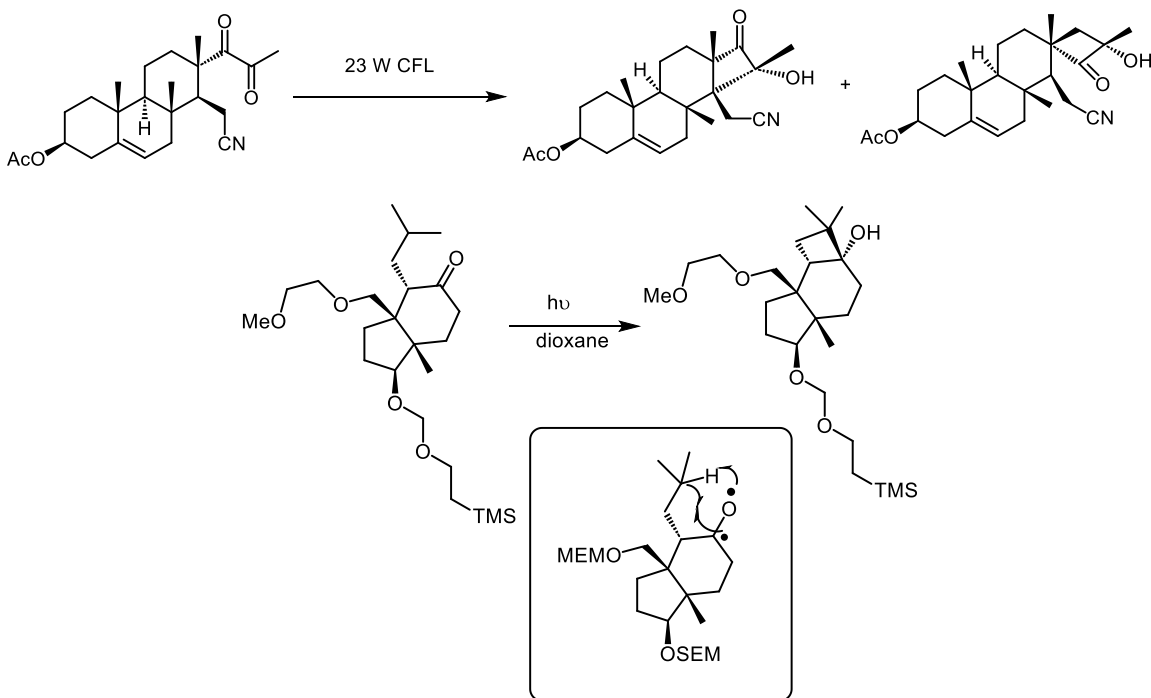
So, we can write them like that once you cleave here that this is up. So, I can write this as a down and this is a up. So, now, if you have a up and down you can see this can form this enol and here you have a down and a up spin that can immediately form this bond. So, that is why this is forming a stereoselective olefin, but once you come to a triplet here. Now, these are the spins. So, this is actually in the same side you can see here because this is a triplet, once you cleave this bond then you can write this as a down and this will be up. That means, in this cases it can form this compound very easily, but the next thing is now there is a spin flipping is required to form this carbon carbon double bond. So, if you remember if there is a spin flipping required then there is a chance of rotation around this bond, this is going to end up giving the mixture of olefin.



Now, there is another example of Yang cyclization here you can see you have this carbonyl group here which is going to the $n \pi^*$ excited states and there it is going to go for this hydrogen atom abstraction here in this case it is going to participate in a radical recombination reaction to form this type of cyclobutanol. There is another example here it is very similar example. I have time to mention here again you see this is the carbonyl group here which actually we can see there is this first it is going to go for this hydrogen atom abstraction here formation of this O dot then formation of this radical here which is going to go for a radical recombination to form this product.



Another example here of course, here also you can see there will be formation of this dot which can abstract the hydrogen from here. So, first it will be the hydrogen abstraction to get to this type of corresponding species corresponding intermediate which can finally go to the corresponding product.



Again, in this conclusion I think I have already talked about the Minisci reaction, I have shown you the Jablonski diagram, I talked about the carbonyl chemistry, how this $n \pi^*$ and $\pi \pi^*$ transition happen, I talked about the Norrish type I and type II and the Yang cyclization. And you can go through this textbook and thank you so much for coming to the class, I am going to see you guys in the next class. Thank you.