Fundamentals and Applications of Supramolecular Chemistry
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Lecture 55

W11L55_Supramolecular Photochemistry and Organocatalysis

Hello everybody, today we are going to discuss further the aspects of supramolecular photochemistry and the photocatalytic reactions that take place in the presence of light.

So, in the previous lecture, we were looking at photodimerization in the case of substituted cinnamic acid, where R is equal to phenyl to start with, and we saw how we can control the dimerization process and preferably get those kinds of products that would not be formed either in solid or in aqueous solution.

But by using a suitable host, we are able to template them in a certain way, such that head-to-head interactions take place, and we get the desired products in sufficiently large yields in cucurbiturils. Now, along the same lines, let us further look at some other interesting examples.

For example, we were looking at uncharged systems, but we can also have charges on the systems. We can have a positively charged species here, and we can also have positive charge here, as well as positive charge here.

Then how are they going to actually come close to each other to dimerize in the presence of a host, for example, the cucurbiturils? So, naturally in the case of cucurbiturils, we can see that you have this molecular vessel. The positively charged species will always be away from each other to minimize the electrostatic repulsion.

If they come together in a way that the positive charges are present, then this is not a favorable orientation. So, we can have dimerization in such a way that the head and tail lead to a head-to-tail dimer.

And what if both species are positively charged? Well, dimerization has also been achieved for systems where protonation happens on both sides. For example, we have NH_3^+, NH_3^+; these species, and when we use cucurbituril, hν, and an aqueous solution, we are able to achieve dimerization.

Positive charges are present, but essentially, they are extensively stabilized by solvation with water molecules. And also, there is a formation of C-C bonds which allows for the stabilization of the compound. So, the interesting thing is that the resulting product is stabilized by extensive solvation, thus leading to the formation of the product.

We can also have the protonation in pyridine-based systems, and under similar conditions, we can again have the photodimerization, where we have pyridinium plus, pyridinium plus, pyridinium plus, and pyridinium plus.

And if you change the position of the nitrogen now, for example, if you consider this one NH+, and this is the para position, this is the meta position which is protonated, then we will have NH+, and here we will have NH+. So, this kind of product will be formed, that is, dimerization takes place, and this is facilitated by pi-pi stacking as well. So, the dimerization of olefins can take place in the presence of suitable host templates, like cucurbiturils. That also talks about the relevance of cucurbiturils.

We previously looked at the dimerization of coumarin in the presence of the diol compounds, and it has also been found that there are different templates that can mediate this dimerization of coumarin.

For example, there have been a lot of applications of Fujita's nano cage, which is the [Pd6L6]12+ cage, the octahedral cage about which we have studied. So, we have the octahedral and palladium atoms sitting here, and these are the ligands present here. Now, in this particular octahedral cage, this is the polar part, and this is the nonpolar part. So, we can have the inclusion of the reactant molecules.

We have the reactant molecules, we have this polar part, and essentially this can now be encapsulated in a large palladium cage. So, this is the encapsulation inside the palladium cage, the palladium nanocage you can see, and this is the polar part, which is in proximity to the palladium center, while the non-polar part is in proximity to the hydrophobic part.

And now this resulting species is stabilized in water, and when we irradiate it, it leads to the formation of a dimer. Look at the stereochemistry; this gives rise to the syn head-to-head dimer. So, these kinds of cages can be formed.

Now you can see that these cages can actually stabilize the reactant molecules, and then the products are formed. This can also be utilized to perform reactions. Palladium nanocages can also be used for the dimerization of coumarins, leading to the formation of the same syn head-to-head dimer.

Thus, this can also be performed. So, we can actually now do this reaction in the presence of the palladium nanocage to give rise to the syn head-to-head dimer.

So, the reactions proceed in a very facile way. And now we can also look at some other applications of solid state photodimerization, where we can consider charge transfer interactions to accommodate the dimerization process.

For example, say we have F5 here; we have F5 here. And this can now dimerize upon irradiation, in the solid state, to give you this F5; this is an F5. So, this is the dimer, and here you can see that there exist charge transfer stacking interactions, which actually drive this dimerization process.

You can extend this to longer olefins. So, you have the two double bonds here, and we can have F5 here, and then again, under similar conditions, it can template the formation of structures.

So, these are the top, then we have this part, and then this part comes down, and then we can have this here. So, again you have got favorable pi-pi stacking. There can be some change in the geometry because the carbon is sp3 hybridized here, but overall, this forms a cage-like arrangement.

So, we have this nice kind of ladder that is formed. Similarly, it has been observed that we can also selectively protonate one end, that is, the pyridine end, to achieve the dimerization of olefins.

So, for example, let us consider this particular reaction, where we have the hydrochloride now, we have protonated the pyridine, and we have the corresponding halogen here, hν, and solid state.

So, this is the head part, this is the tail part, so this will become my pyridinium H+, this is the aryl tail part, and this is my protonated pyridine; this is the head part. And now there are favorable interactions between this protonated pyridine and that of the aryl group.

So, this leads to the formation of an anti-head-to-tail dimer. It is also to be kept in mind that the unprotonated compound does not react at all. So, we can take another example of this where we extend it to NH+, hν, solid state. This will now lead to the formation of the anti-head-to-tail dimer.

So, in this way, we are able to have dimerization processes, and we have also been able to achieve the formation of 4-membered cyclobutane rings by this process in a facile one-step dimerization.

Let us take this particular reactant. It has been observed that it undergoes dimerization. So, you can see that it forms this four-membered cyclobutane ring and the spiro system as well, the di-spiro system.

So, the [2+2] dimerization leads to the formation of this kind of photo adduct, and photodimerization has also been very useful in achieving chiral induction in crystals, starting from optically active materials.

So, we can start by obtaining chiral crystals using the concept of photodimerization.

Let us begin with this example. This is the four-membered ring. We can now see that this particular chiral product has been formed. So, now when R1 = 3-pentyl and R2 = methyl, the enantiomeric excess is 100 percent; when R1 = 3-pentyl and R2 = propyl, it is 80 percent.

So, now you can see that in this case, we have an achiral olefin, giving rise to a chiral photo-dimer with 100 percent ee, and this is achieved by topochemically controlled dimerization.

So, this process, you can see, the topochemical control, is so useful that we are able to achieve chiral products from an achiral olefin. And when the crystal structure was determined, it was observed that it crystallizes in a chiral space group, which is proof of the existence of chirality.

On the contrary, when you take these olefins in solution, they simply racemize. So, this is the difference. In a solid state, you have a chiral product, but in a solution, they simply racemize.

We can take another example of chiral induction. Here, you can see that the reaction occurs between this double bond and the particular double bond on the other side. The double bond on the pyridine side reacts with the double bond on the carboxylate side to give you the photodimer, in 92 to 95 percent enantiomeric excess.

Similarly, photodimerization has also been achieved on different kinds of surfaces, like clay, zeolites, silica, etc. One such example on a silica surface is that you can take this particular compound.

So, you have the favorable $\pi...\pi$ stacking here, and we can get the corresponding trans product as well. So, supramolecular photochemistry has also been used to achieve the stabilization of reactive intermediates via encapsulation in large-curved molecules.

And one such example of a molecule that has a curved architecture and can actually stabilize these reactive intermediates, which otherwise are very reactive in the gas phase or in solution, is hemicarcerands.

So, the hemicarcerand's overall shape is like this, and this cavity has both hydrophobic content as well as hydrophilic content, but by and large, it is a very compact molecule, having a closed shape, and therefore it is able to stabilize reactive molecules.

For example, if we have this particular molecule, in the presence of light, it will form cyclobutadiene plus carbon dioxide, and this can be stabilized. So, normally the short-lived species that actually exist for a few microseconds can be stabilized for a period of days, weeks, or months inside these hemicarcerands.

So, for example, cyclobutadiene can be stabilized.

Then we can take another example of butenedione. Please keep in mind that we always have the hemicarcerand, a large bulky cyclic curved molecule, which has a cyclic curvature. And when we irradiate with light greater than 400 nm, it forms a species, and then with hν greater than 300 nanometers, it forms benzyne.

So, you can stabilize benzyne inside the hemicarcerand, and you can also stabilize radical species. This is present, for example, in a cyclodextrin, and we can have the reaction where we will have cleavage of this bond.

It is a photolytic dissociation in the presence of hν. So, it forms this particular free radical, and this free radical inside this cyclodextrin can be stabilized for days.

Normally, this is stable for a very short time or a few microseconds. So, it can be stabilized, and similarly, we can generate a radical cation. So, we can have a radical cation that is generated.

And then, with this radical cation, you can stabilize it for months, okay? So, with the double bond, you have two electrons; if you remove one electron, you just have the odd electron, which is the radical cation.

Similarly, you can consider this particular compound, and it can undergo photolytic dissociation, Ph2-CH, for weeks; and then if it loses an electron, Ph2-CH+, you can stabilize this as well.

Another example we can consider is the diazo compound. You have this kind of cyclic strained system; in the presence of light, in dichloromethane, it forms this particular species called carbenes. It forms a carbene, which can be stabilized for days inside the hemicarcerand.

So, we have to keep in mind that all these are being done in the presence of a host, and this association actually inside this cavity stabilizes these reactive intermediates. So, overall, as we see, there are a lot of interesting applications of photochemistry.

To summarize, one last very important application of photochemistry is in the field of supramolecular organocatalysis. And I will give you one specific example of a depiction of supramolecular organocatalysis. For example, let us take this particular compound, which is again a derivative of coumarin, and irradiate it with 350 nanometers in the presence of an organocatalyst.

I will tell you the structure of the organocatalyst. For a period of 2 hours, it can give rise to this particular enantiomer and then the mirror image of this particular enantiomer. So, we have the mirror image of this particular enantiomer.

We have this X here; X is equal to hydrogen, fluorine, -OMe, and methyl. And so, these enantiomers are obtained; the possibility exists that these two enantiomers are obtained, and what has been utilized is a binaphthyl-based thiourea as an organocatalyst.

So, we have this particular structure; we have already seen the applications of thiourea, but this is a modified thiourea, where we have electron-withdrawing groups here, and we have the binaphthyl ring here, which interacts by hydrogen bonds with the oxygen. So, this is the transition state-like geometry, and this comes from the upper face.

So, when you have the planar face of the coumarin, the hydrogen bonding is strong from one side of the organocatalyst, and therefore, the other face is now exposed, over which this double bond can come and possible photodimerization can now take place.

So, here you can see now that the photodimerization can take place in an enantioselective fashion, so that one enantiomer is preferably formed, and what was achieved is specifically when you have -CF3 here.

You normally have electron withdrawing groups here, but in this case, you have electron withdrawing groups here as well.

However, you can actually have a different set of combinations, different kinds of catalysts with electron donating as well as electron withdrawing groups, which will optimize the reactivity of this catalyst.

And what was observed is high enantioselectivity, in the range of 77 to 96 percent ee, in the photoproduct when 1 to 10 mole percent of the organocatalyst was used.

It was also observed that this particular reaction can be scaled up to large quantities, and during the process of scale-up, the enantiomeric excess is large, almost 96 percent, and the yield of the reaction is around 77 percent.

So, this talks about the power of organocatalysis, which is actually mediated by hydrogen bonds that bring about the necessary enantioselectivity.

So, I hope that overall, in this particular module this week, you have been able to appreciate the relevance of supramolecular catalysis, supramolecular reaction barrels, supramolecular photocatalysis, and all these important and interesting aspects of supramolecular chemistry.

In the next week and the last week, we are going to look at some important applications of supramolecular chemistry in other systems as well.

Thank you.