

Principles and Applications of Enolate Alkylation: A Unique Strategy for Construction of C-C (sp³ - sp³) bonds in asymmetric fashion

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Module - 01

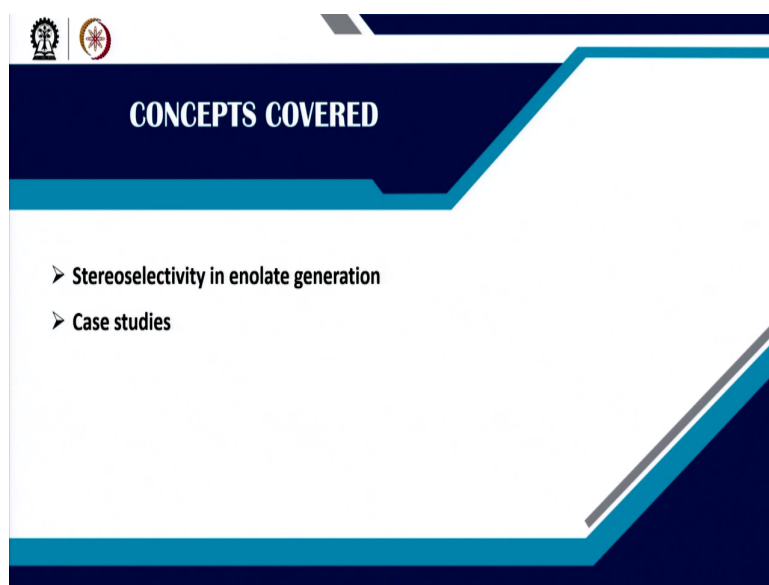
Basic introduction of enolate

Lecture - 04

Different mode of asymmetric induction in enolate alkylation

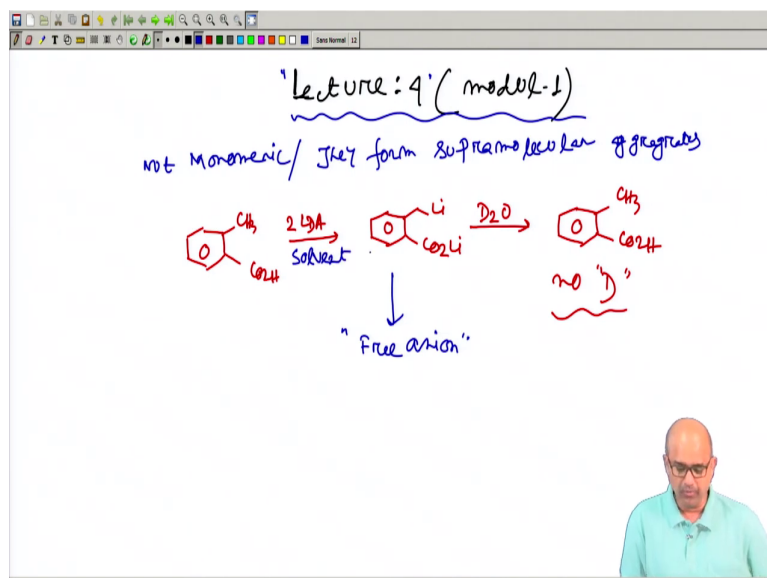
Welcome back students. So, basically we are discussing this Principles and Application of Enolate Alkylation.....

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today we will be talking about the lecture 4 in our module 1, and mainly the content which we will be covering today, the stereoselectivity in enolate generation. And subsequent case studies and particularly the stereoselectivity in enolate generation was very important concept and which will be required for us in the subsequent section to understand the origin of asymmetric induction in better way.

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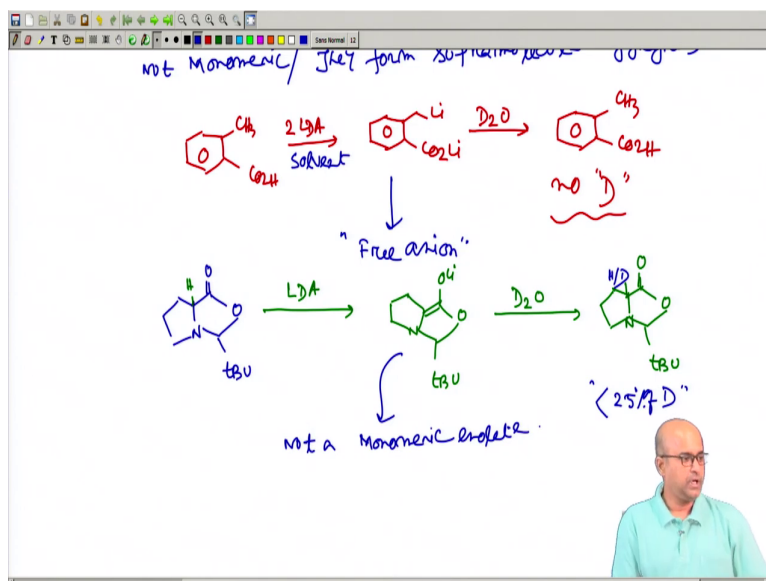


In the last class we talked about that how this enolate, different kind of enolate can be generated and what are different aspects the structural aspects and I said that enolates usually are not monomeric. They form supramolecular aggregates, they are not monomeric they form supramolecular aggregates and mainly the formation of supramolecular aggregates has been proven by different analytical techniques, such as low temperature X-ray and low temperature NMR technique.

In addition, some of the scientists also proved by experimental technique that supramolecular aggregate formation in the enolate chemistry really happens. Let us talk about one of such example, this compounds name is toluic acid which all of us are quite familiar, toluic acid if you use two equivalent of LDA. So, usually the benzylic proton will be deprotonated you get CH_2Li and this carboxylic acid how about repeat we get CO_2Li .

And now if this compound you use D_2O , you find that it will get back to the original compound, but no deuterium incorporation took place. So, what does it mean? It means that the carbon ion or this enolate this is basically a lithium salt, it's not a free enolate or free anion. This is basically probably form say multi molecular or supra molecular aggregates with some solvent or other additive.

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On the same way, other people also have been proven or tried to have try to support some experimental evidences, one such experimental evidences we will be discussing here. This is kind of a cyclic amide where this hydrogen seems to be acidic and you initially treat this compound with LDA.

So, initially you can get the corresponding enolate this O -Li -O these things tertiary butyl ok. Now, if we treat this compound with deuterium oxide, same like earlier it has been found that here also deuterium incorporation takes place, but in very less amount. So, write down the structure of this entire compound and you will find that this deuterium or hydrogen I mean it either hydrogen or deuterium.

And you found this compound you will basically get less than 20 percent, 5 percent of deuterium incorporation. So, what does it mean? It means that this enolate is not a monomeric enolate, it's not a monomeric enolate and usually exists as a supra molecular aggregation and that basically helps to give you a better understanding about the enolate structure.