

School of Basic and Applied Sciences

Course Code : MSCH6001

Course Name: Photochemistry & Pericyclic reaction



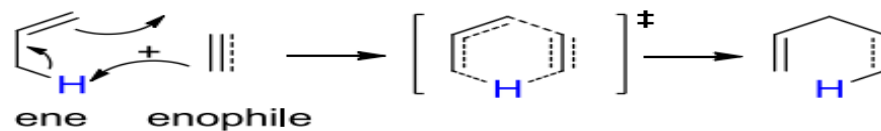
Presentation on the Ene-reaction with it's concerted mechanism, regioselection and advantages

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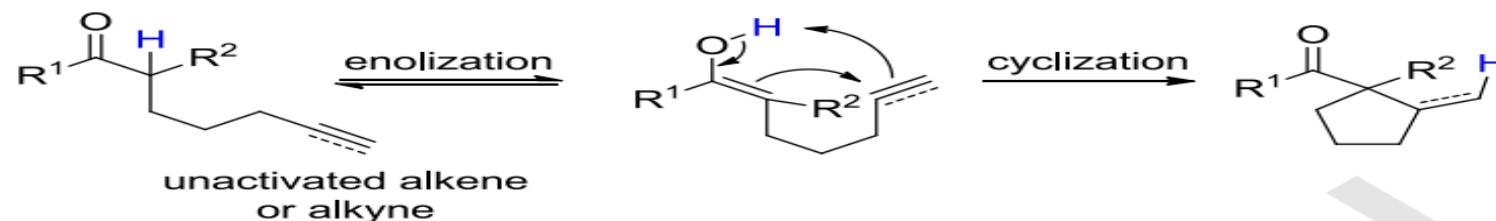
Introduction:-

- The joining of a double bond or triple bond to an alkene reactant having transferable allylic hydrogen is called ene reaction.
- The allylic hydrogen undergoes 1,5-migration with change in the position of the allylic double bond. Like Diels Alder reaction, it is also 6 pi electron electrocyclic reaction.
- As a representative example of this class, Conia-ene reaction was first presented by Conia and Le Perchec in 1975 [2], referring to the thermal cyclization of unsaturated carbonyl compounds bearing an alkenyl or alkynyl moiety via an enolization process.

a) Typical ene reaction



b) Thermal Conia-ene reaction



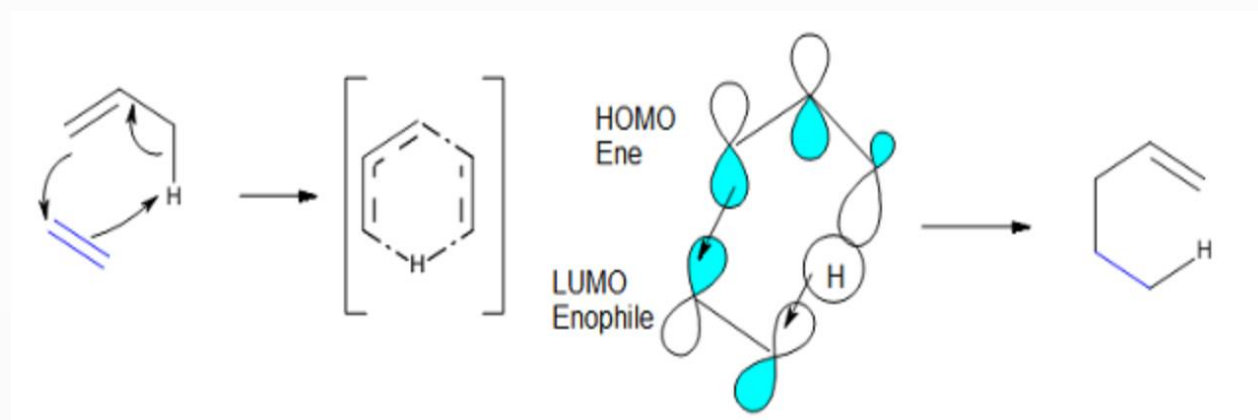
- Many useful Lewis acid-catalyzed ene reactions have been also developed, which can afford high yields and selectivities at significantly lower temperatures, making the ene reaction a useful C–C forming tool for the synthesis of complex molecules and natural products

Concerted mechanism for the ene – reaction

- 1) The main frontier-orbital interaction occurring in an ene reaction is between the HOMO of the ene and the LUMO of the enophile.
- 2) There is concerted all-carbon-ene reaction, in general, a high activation barrier, which was approximated at 138 kJ/mol in the case of propene and ethane
- 3) The order of barrier decreases along the enophiles in the order $\text{H}_2\text{C}=\text{CH}_2 > \text{H}_2\text{C}=\text{NH} > \text{H}_2\text{C}=\text{CH}(\text{COOCH}_3) > \text{H}_2\text{C}=\text{O} > \text{H}_2\text{C}=\text{PH} > \text{H}_2\text{C}=\text{S}$, as the reaction becomes more and more asynchronous and/or the activation strain decreases.

Regioselection

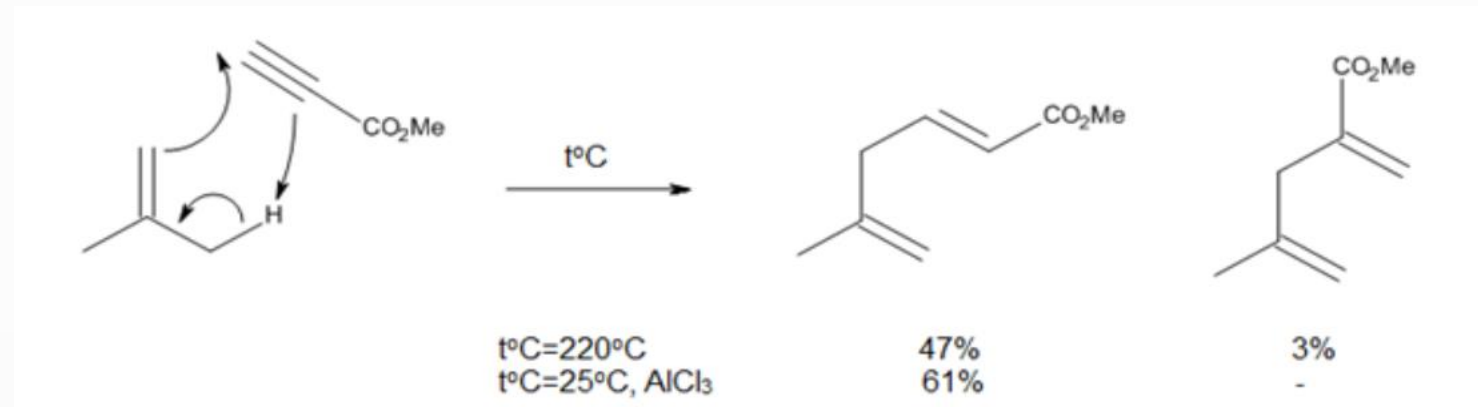
- Ene - reaction is largely determined by the steric accessibility of the ene allylic hydrogen.
- Methyl and methylene H atoms are abstracted much more easily than methine hydrogens.
- In thermal ene reactions, the order of reactivity for the abstracted H atom is primary > secondary > tertiary, irrespective of the thermodynamic stability of the internal olefin product.



Advantages

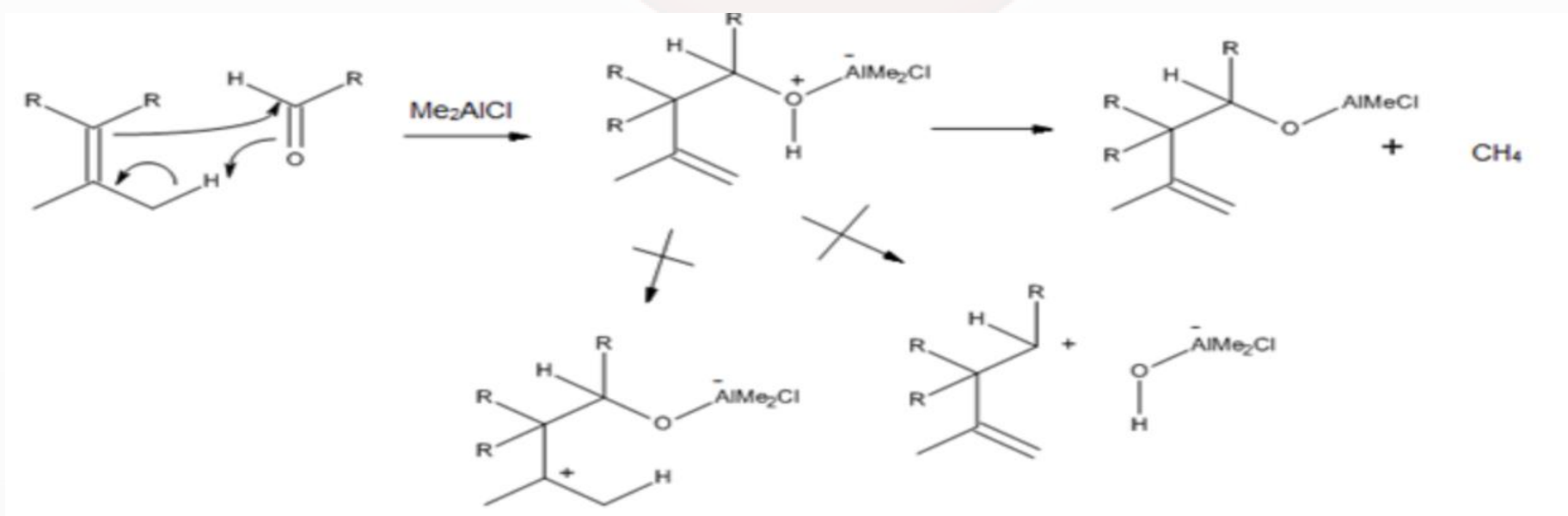
- proton-catalyzed olefin polymerization or isomerization reactions.
- Since enophiles are electron-accelerate the ene reaction, as it occurred for the reaction

Fig:- Improvements brought to the ene reaction by Lewis acid catalysis



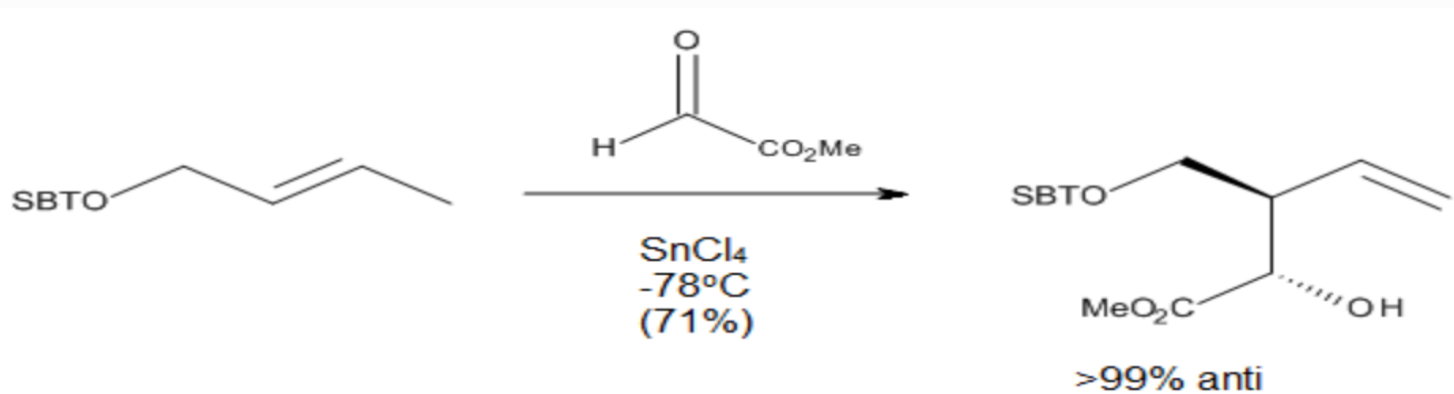
- 1) Alkylaluminum halides are well known as proton scavengers, and their use as Lewis acid catalysts in ene reactions. Lewis acid can directly complex to a carbonyl oxygen.
- 2) Trialkylaluminum catalysts have been developed for enophiles that contain a C=O bond.
- 3) It was found that Me_2AlCl is a very useful catalyst for the ene reactions of α,β -unsaturated aldehydes and ketones, as well as of other aliphatic and aromatic aldehydes.
- 4) The ene-adduct- Me_2AlCl complex can further react to afford methane and aluminum alkoxide.

Fig:- Me_2AlCl -catalyzed carbonyl-ene reactions



- In the case of directed carbonyl-ene reactions, high levels of regio- and stereo-selectivity have been observed upon addition of a Lewis acid, which can be explained through chair-like transition states
- Some of these reactions can run at very low temperatures and still afford very good yields of a single regioisomer.

Fig:- Lewis acid catalyzed, directed carbonyl-ene reaction



CONCLUSIONS:-

There is formation of new C-C and C-H bonds no rings formed in this reaction. Conia-ene reactions, as a type of ene reactions, have not become a remarkable focus until the beginning of 21st century, Conia-ene reactions have gained great significance in synthetic chemistry due to their high efficiency and atom economy on the construction of valuable cyclic molecules. In ene-reaction, the activation energy is greater than the Diels-Alder reaction and conia-ene reaction and high temperature are generally required to the ene-reaction. The Lewis acid catalyzed reactions afford high yields and selectivity at significantly lower temperatures, making the Ene Reaction a useful C-C bond forming tool for the production of intricate molecules and natural products.

REFERENCES

- Fernandez, I.; Bickelhaupt, F. M. (2012). "Alder-ene reaction: Aromaticity and activation-strain analysis". *Journal of Computational Chemistry*. 33 (5): 509–516. [doi:10.1002/jcc.22877](https://doi.org/10.1002/jcc.22877). [PMID 22144106](https://pubmed.ncbi.nlm.nih.gov/22144106/)
- Snider, B. B. (1980). "Lewis-acid catalyzed ene reactions". *Acc. Chem. Res.* 13 (11): 426. [doi:10.1021/ar50155a007](https://doi.org/10.1021/ar50155a007)
- Paderes, G. D.; Jorgensen, W. L. (1992). "Computer-assisted mechanistic evaluation of organic reactions. 20. Ene and retro-ene chemistry". *J. Org. Chem.* 57 (6): 1904. [doi:10.1021/jo00032a054](https://doi.org/10.1021/jo00032a054). and references therein