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Review Article

Clay Catalyst in Organic Synthesis

Kush Vijaybhai Darji*

Chemistry Department St. Xavier's College (Autonomous), Ahmedabad-380009.

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ABSTRACT

Clay and Modified clays are very useful for different type of reaction, like FC-alkyalation, Rearrangement, oxidation, Nitration, Esterification, Reduction etc. Clays are react as Acid or Base like Bronstate and Lewis Acid or Base. Clay has both characteristics acid & base. Catalyst having good surface activity, cationic-anionic ion exchange capacity. There are some reaction and how it occurs given here.

INTRODUCTION

Clay catalyst is a particularly clay-based catalyst. That clay based catalysts are found from naturally or synthetically. Clays are a class of soil with particular size of <2mm in diameter. This type of catalyst are widely used in different type of industries for their unique property, such as high surface area, ion exchange capacity and thermal stability. Clay catalysts are solid acidic catalyst which can function as both Bronstet & Lewis acid in their natural and ion exchange form.[10] Clay catalysts are materials made from natural clay minerals that have unique properties, making them useful for speeding up a variety of chemical reactions in organic synthesis. These clay minerals consist of layers of silicate and aluminum, which give them their special characteristics. Due to their layered structure and high surface acidity, clay catalysts are particularly effective in promoting reactions like alkylation, rearrangements, and oxidations. The introduction of this document discusses the composition and structure of these clays, highlighting their ability to facilitate chemical transformations through both their acidic sites and the unique arrangement of their layers. This makes them a versatile tool in the field of green chemistry, providing an environmentally friendly alternative to traditional liquid acids.[7]

Natural Clays:

***Corresponding Author:** Kush Vijaybhai Darji
Address: Chemistry Department St. Xavier's College (Autonomous), Ahmedabad-380009.
Email : KUSHDARJI26@GMAIL.COM

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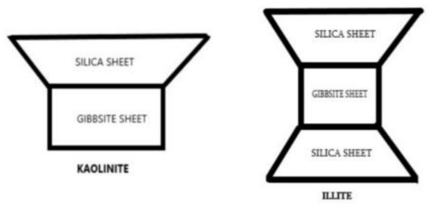
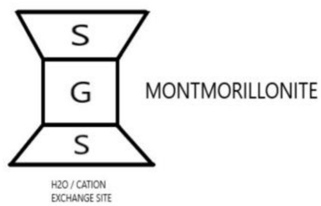
There are 3 type of natural clays. Kaolinite, Illonite and Montmorillonite. They all are made up from two sheets, that one sheet is gibbsite sheet and second is silica sheet. Gibbsite is [$Al_2(OH)_6$] and Silicate is $[SiO_4]^{4-}$. Gibbsite sheet is Octahedral in shape and Silica sheet is Tetrahedral in shape.[3]

(1) Kaolinite: This clay made up from one gibbsite sheet and one silica sheet. It's a common type of clay.

(2) Illonite : It looks like sandwich type of clay. Up side and lower are made up from silica sheet and in middle sheet is gibbsite sheet..

(3) Montmorillonite : It's similar to the illonite, but it has a water ion exchange capacity, cation exchange capacity. In this type of clay in between consecutive sheet has we can insert metal ion to make favorable catalyst and this used to make modified or synthetic clays. For that it is widely used catalyst.





There are the figure of natural clays, how arrangement of sheet shown in figure. Clay catalysts are natural or modified clay minerals used to accelerate chemical reactions. Montmorillonite, a type of smectite clay, is one of the most widely studied because of its ability to exchange cations (positively charged ions) and its swelling capacity, which allows it to accommodate various molecules between its layers. This ability to modify its structure makes montmorillonite an excellent candidate for use as a catalyst in various organic reactions.[11] Clay catalysts are valued for their low cost, high availability, and eco-friendliness. They offer several advantages over traditional catalysts. Clay catalysts can be modified to enhance their properties, making them suitable for a wide range of chemical reactions. Environmental Benefits: Being natural materials, they are less harmful to the environment compared to synthetic catalysts.

Reusability: Clay catalysts can often be regenerated and reused, which contributes to sustainable industrial processes.

#Modified/Synthetic Clays:

(1) **Acid activated clays**: In this clay, clays are treated with acid to increase their surface area and enhancing catalytic activity.

(2) **Organoclays**: This type of clays is modified with organic compound to improving compatibility with organic reactants.

(3) **Pillared Clays**: This type of clays is modified with intercalating metal oxide. That oxide inserts between clay layers to create stable structures with large surface areas. Clay catalyst has huge application in different ways like petrochemical industry (catalytic cracking of petroleum fraction to produce lighter

hydrocarbons like gasoline), environmental application (wastewater treatment, air pollution control reduce emission of harmful gases), agriculture(fertilizer production), chemical synthesis(acid-base catalysis, green chemistry).[2]

Pillared Clays: Pillared clays or PILCs, are material that have become increasingly interesting recent year. These materials are created by inserting large molecules between the layers of clay, which helps to keep layer apart and creates tiny pores in the structure. These pores are important because they can be used in various chemical process, such as catalysis. Researcher have developed many different method to make these PILCs and to study their properties. Researcher found new ways to control the size of the pores and have developed better method to measure them. These new method and they help us to understand the structure of these clays better.[19]

K10 Montmorillonite: In particular montmorillonite clays most used montamorillonite is K10. K10 is a type of clay that has gained a lot of attention in the field of chemistry, especially in catalysis, which is the process of speeding up chemical reaction. This clay is popular because it is low cost and environmentally friendly. It has some special qualities, like the ability to exchange ion and to expand, which allows it to host different substance between its layers. K10 works as solid acid catalyst and as a support for metals and other substance in various organic reaction. [16] Clays like K10 montmorillonite are often used as solid acid catalysts in reactions such as rearrangements, isomerizations, and condensations. Their acidity can be enhanced by exchanging the natural cations with more acidic metal ions.[16] Support for Metals: Montmorillonite can also act as a support for metal nanoparticles or complexes, providing a stable platform that enhances the catalytic activity of these metals. [20]

KSF catalyst : KSF catalyst is a special type of material made from clay, specifically designed to speed up certain chemical reactions. It's commonly used in organic chemistry, particularly for a reaction called "Friedel-Crafts alkylation," which is important for making various chemicals, including those used in plastics and dyes.[20]

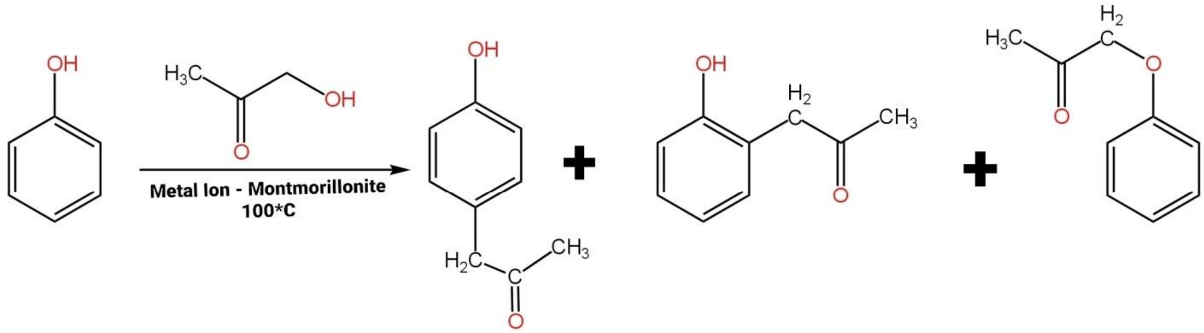
This catalyst is created by treating a type of clay (bentonite) with acids. The acid treatment changes the clay's structure, making it more effective in these chemical reactions. The main features of KSF catalyst include; KSF catalyst is acidic, which is crucial for its ability to promote chemical reactions. The acidity comes from certain parts of the clay that can donate or accept protons (like hydrogen ions), helping to break down or form chemical bonds.[20]

Overall, KSF catalyst is valuable in industrial chemistry for making complex organic compounds more easily and with better environmental outcomes compared to using traditional liquid acids. [20].

Clay Catalyst in Organic Synthesis:

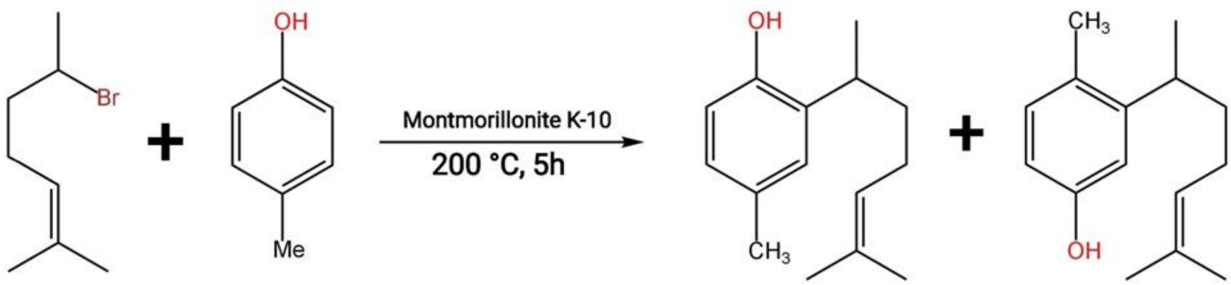
There are many applications of clay catalyst in organic synthesis, like friedel-craft alkylation, acylation, rearrangement, nitation, oxidation, reduction, acetal formation, esterification, etherformation, etc. so many organic reaction will happen in presence of clay catalyst.

(1) Fridel-Craft Alkylation:



•FRIEDEL-CRAFT ALKAYLATION

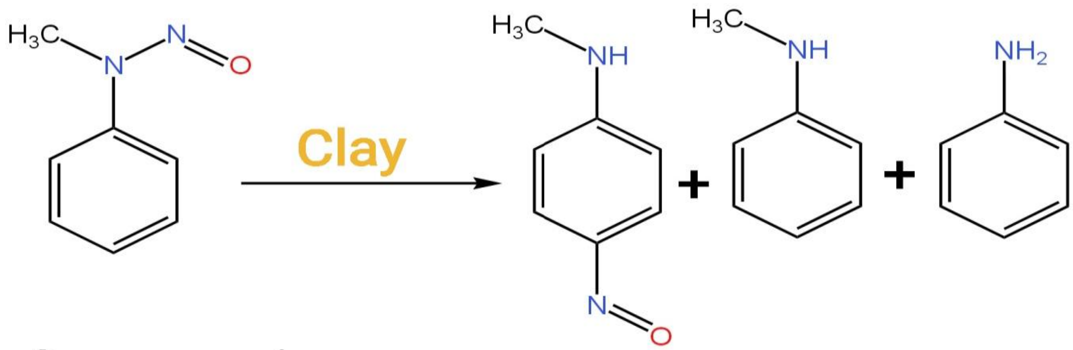
In this reaction phenol or anisole is treated with hydroxyacetone (1-hydroxy acetone) in presence of metal ion clay to produce several pharmaceutically active compound. This reaction occurs in mild condition with less water.[7]



Alkylation

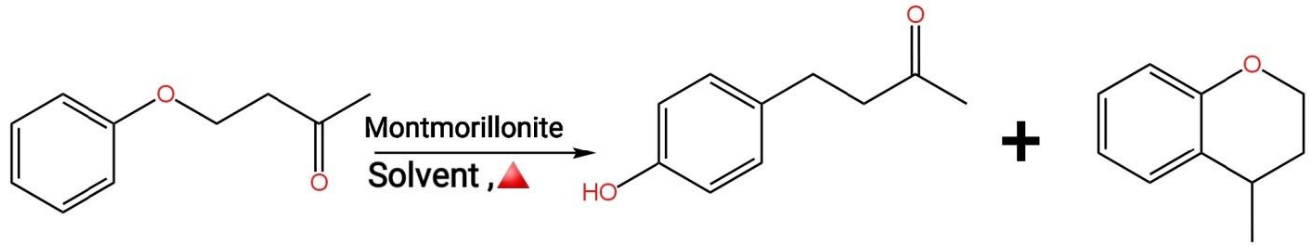
That particular alkylation of p-methylphenol with 6-bromo-2-haptene using K-10 montmorillonite catalyst to get natural product Elvirol. In this alkylation reaction alkyl group compound (bromoheptene) is directly attach with aromatic ring with loss of HBr. Temperature required for this reaction is 200 C for 5 hours. [1]

(2) Rearrangement:



Rearrangement

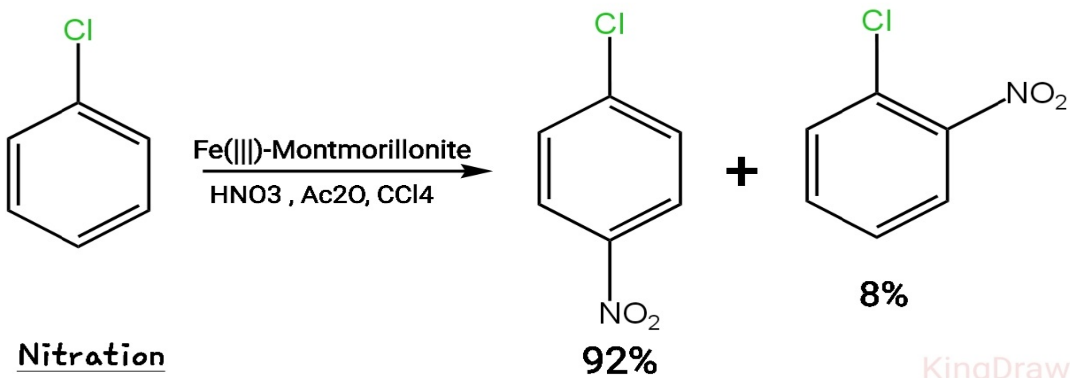
N-Nitoso-*N*-methylaniline undergoes the rearrangement in presence of clay then product Nitroso-*N*-methylaniline was found a major product along with *N*-methylaniline. That rearrangement product predominates under polar protic solvent. [7]



Rearrangement

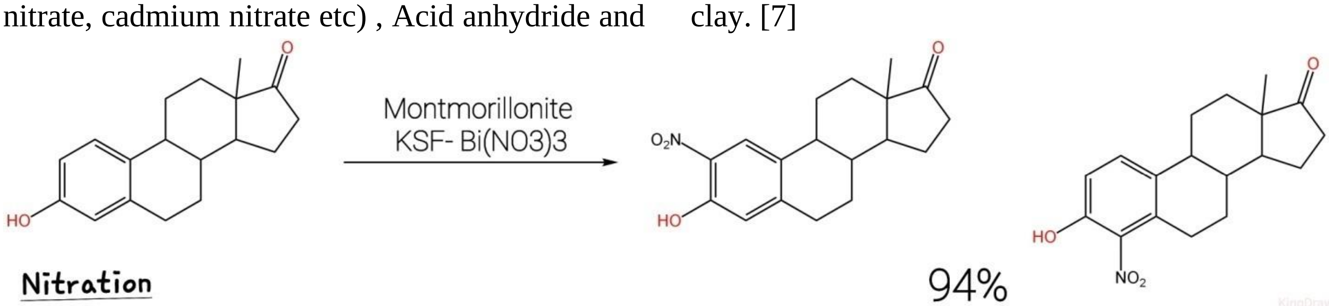
Similarly, ether was rearranged to ketone type product. In this rearrangement Zn-montmorillonite was most effective catalyst. 1st product will found 16-24% and 2nd will found 3-4%. [7]

(3)Nitration:



Nitration

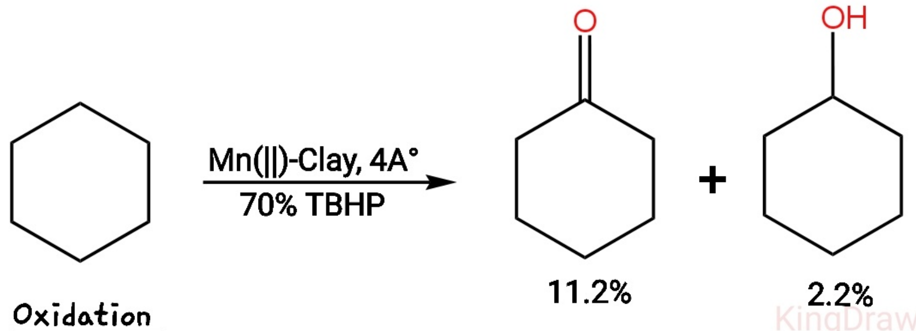
Nitration of aromatic compound can be carried out with high yield using nitric acid and modified montmorillonite clays. *Fe*-Montmorillonite clay was most effective for para-position selective substitution. This reaction occurs in presence of metal nitrate (like Bismuth nitrate, aluminium nitrate, cadmium nitrate etc) , Acid anhydride and an Organic solvent (like Chloroform, Carbon tetrachloride, DCM). Fe-Montmorillonite is give para selective product at high amount of yield approx 92%. The use of transition metals (pillared clay) has gives 92% para selective product. That type of clay we can say Fe-acid activated pillared clay. [7]



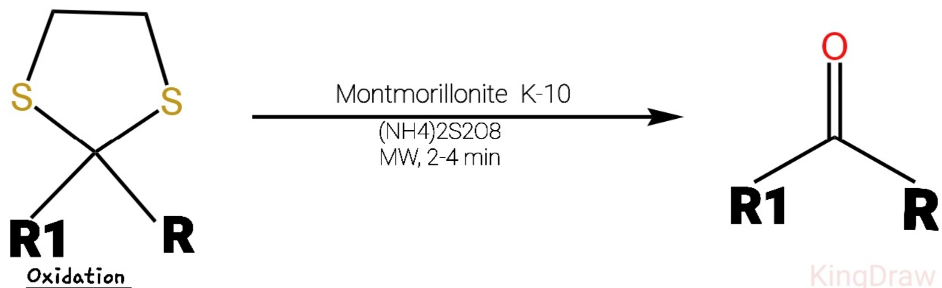
Nitration

In above nitration process to get high yield using bismuth nitrate supported on KSF. Nitro group attach at aromatic ring, that also called aromatic nitration.[1]

(4) Oxidation:

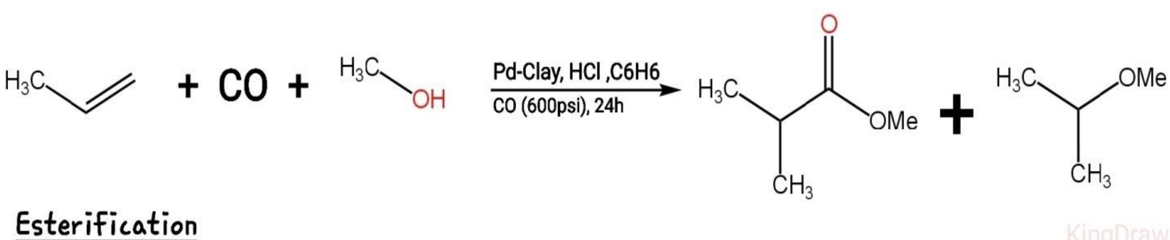


Oxidation of alkanes such as cyclohexane, cyclooctane, octane with 70% tert-butyl hydroperoxide(TBHP) in presence of Mn-clay as catalyst and 4Ǻ molecular sieves product the corresponding ketones and alcohols.[7]



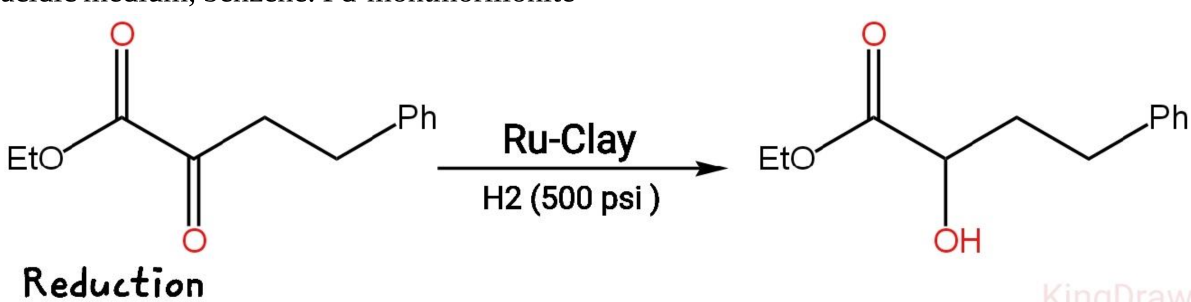
1,3-dithianes under goes reaction with ammonium persulphate with montmorillonite K-10 & microwave irradiation to get appropriate keton similar to reactant.[1]

(5) Esterification:



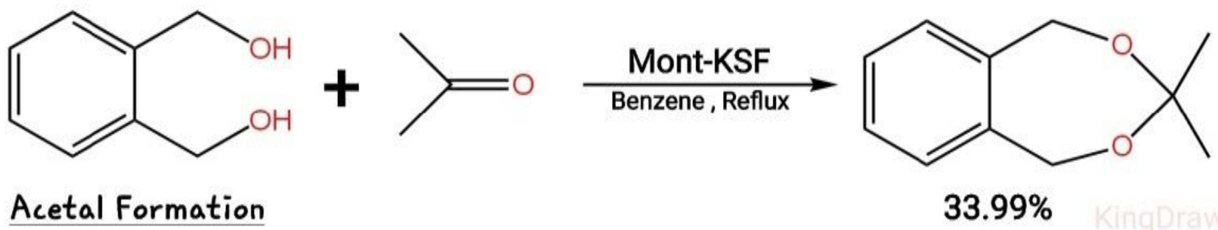
This process developed for preparation of methyl acetate. Methyl acetate was prepared by using methanol. This reaction occurs in presence of Pd-clay, acidic medium, benzene. Pd-montmorillonite acts as efficient catalyst for alkoxyformaylation of olefins with CO and Methanol to get ester.[7]

(6) Reduction:



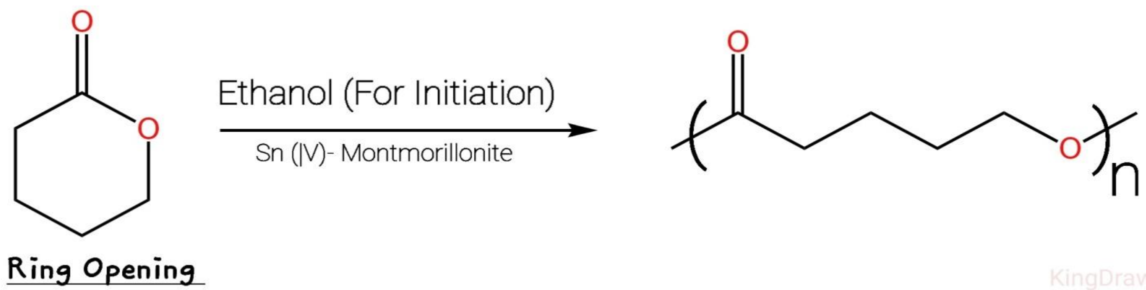
Ruthenium Clay, prepared by the reaction of RuCl₃·xH2O with 3-phosphinopropyl function alized fluka K10 montmorillonite, is an effective catalyst for the reduction α-ketoesters, to get 50-89% yield. α-ketoester is reduced by hydeogen at 500psi in presence of Ru-clay to give 87% yield.[7]

(7) Acetal Formation:



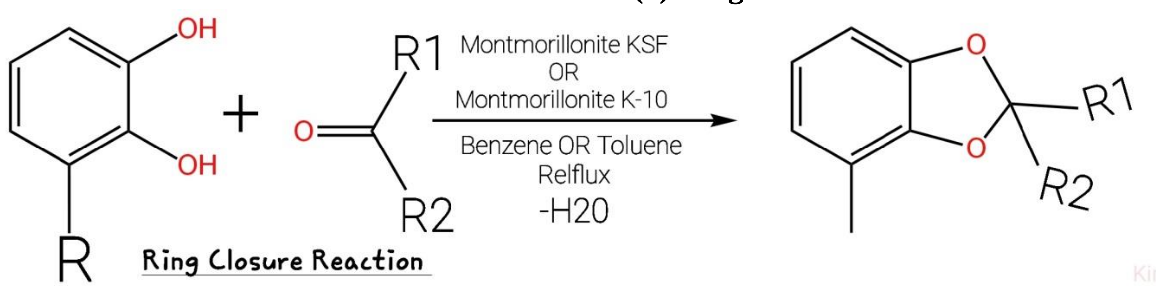
Diol reaction with carbonyl compound to produce1,5-dihyro-3H-2,4-benzodioxepines in high yields has been described by using KSF catalyst.[7]

(8) Ring Opening Reaction:



This is polymerization reaction. This reaction controlled by Tin (|V)-montmorillonite, ethanol is used for initiation of reaction. Starting material used in this reaction is δ –valerolactone. [1]

(9) Ring Closure Reaction:



In this reaction both starting material combined together and form ring, in that reaction aromatic ring combined with ketonic compound and create 5 member ring. R should be H or OH, R1 & R2 should be H, methayl, benzene, alkyl chain, etc. Product found is 2,2-disubstitued-1,3-benzodioxoles [1].

(10) Hydroboration:

This reaction occurs in presence of [Rh(COD)(R)-(BINAP)]BF4 complex on Montmorillonite K-10. Rhodium complex is newly developed clay catalyst. For boration we used catecholborane, and found yields upto 89-97%. [1]

Advantage of Clay Catalyst in Organic Synthesis:

1) High surface area and porosity.
2) Versatile Acid-Base properties. (modified acid-base catalyst)
3) Thermal Stability.
4) Environmental friendliness.
5) Cost-effective.

CONCLUSION:

Clay catalyst is used widely in different organic synthesis. It also used in natural product synthesis like Synthesis of Flavonoids, Terpenoids, Steroids, Alkaloids etc. Clay catalyst have proven to be versatile and efficient in synthesis of organic & natural products. Their ability to catalyze a wide range of reaction under mild condition, coupled with their environmental and economic benefits. Now industry also focused on Green Chemistry and sustainable synthesis methods. Clay being inexpensive, readily available and reusable solid catalyst, show tremendous potential for many industrial reaction such as nitation, alkylation, oxidations, reductions, etc asymmetric catalysis using clays as catalyst holds promising future work.

Future Scope & Challenges:

In future is very high scope of clay catalyst. That catalyst acidity is higher than zeolites, and their mechanical properties are better than acidic ion exchange resins, they are considered as the environmentally beginning acid catalysts of the future.

Challenges: Natural variability of clay, Purification, Large scale production etc.

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