

Organic Synthesis using Clay Catalysts

Clays for 'Green Chemistry'

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Gopalpur Nagendrappa teaches organic chemistry at Bangalore University. His work includes organic synthesis and reaction mechanisms mainly in the area of organosilicon chemistry. Presently he is also working on organic synthesis under solvent-free conditions and using clay-catalyses.

Care for the Environment and Community

One of the major current challenges before chemists is to develop synthetic methods that are less polluting, i.e., to design clean or 'green' chemical transformations. The chemical manufacturing processes should be such that they do not cause permanent damage to the environment or disturb the ecological balance. Ways to minimize the consumption of energy and raw materials used in synthesis must be devised so that optimal value of resources could be realized. Thereby environmentally benign products are obtained at affordable costs. Such a concept, though not new, has received enormous attention in recent times. The desire to make chemical manufacturing environmental friendly is not a new one. Such awareness was there even among the nineteenth century chemists, industrialists and lawmakers. The problem has become more acute in recent times and has received wider attention because of our better understanding of the causes of environmental degradation. Industries and scientific organizations have put clean technology as an important R & D concern. The area of chemistry, which is particularly directed to achieve such goals, is termed as 'green chemistry' and is defined, according to an US award programme, to be one that 'encompasses all aspects and types of chemical processes – including synthesis, catalysis, analysis, monitoring, separations and reaction conditions – that reduce impacts on human health and the environment relative to the current state of the art'.

The Chemists' Role in Reducing Pollution

Chemists are playing a major role in mitigating the problem of pollution, at least in part, by tackling them at source. For

Keywords

Montmorillonite, ion-exchange, clay-nanomaterials, dehydration pyrolysis, rearrangement, steric control on clay, pollution-free chemistry.

example, two problems of global proportions that have been worked out with a fair degree of success by chemists are (1) the reduction of pollution from automobile emission by developing catalytic converters for motor cars and (2) the synthesis of alternative chemicals for replacing fluorochlorocarbons used in refrigeration equipment.

Efforts to realize the objectives of making chemical manufacturing ecologically benign are being made at different stages of reaction sequence in the laboratory synthesis or industrial production. For example,

1. Developing milder reaction conditions like (a) avoiding strong acids or bases and other corrosive media and (b) bringing down reaction temperature and pressure.
2. Reducing the number of steps in a reaction sequence.
3. Formulating more efficient isolation and purification procedures.
4. Replacing hazardous or expensive reactants and reagents by safer and economical ones.
5. Developing solvent-free processes or minimizing the use of solvent or using solvents that can be quantitatively recovered at low cost.
6. Devising stereo- and regio-selective synthetic procedures.

In addition, many other possibilities to modify a preparative sequence are likely to be found in individual cases.

Catalysts for Controlling Pollution

In achieving many of these goals, catalysts help the synthetic chemist in a big way. Catalysts could be simple or complex, synthetic or natural chemicals, which are capable of making an otherwise impracticable reaction to occur under the mildest possible conditions. An important family of catalysts that has received considerable attention of the synthetic chemist in recent times is derived from the soil, the most noteworthy ones being clays and zeolites.

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Clays are a class of soil with a particle size of <2 mm in diameter ($\sim 7.2 \times 10^{11}$ particles per gram of clay, which implies a surface area of about 23000 cm^2 per gram) they are crystalline hydrous aluminosilicates, and also contain various other cations.

The Nature of Clays

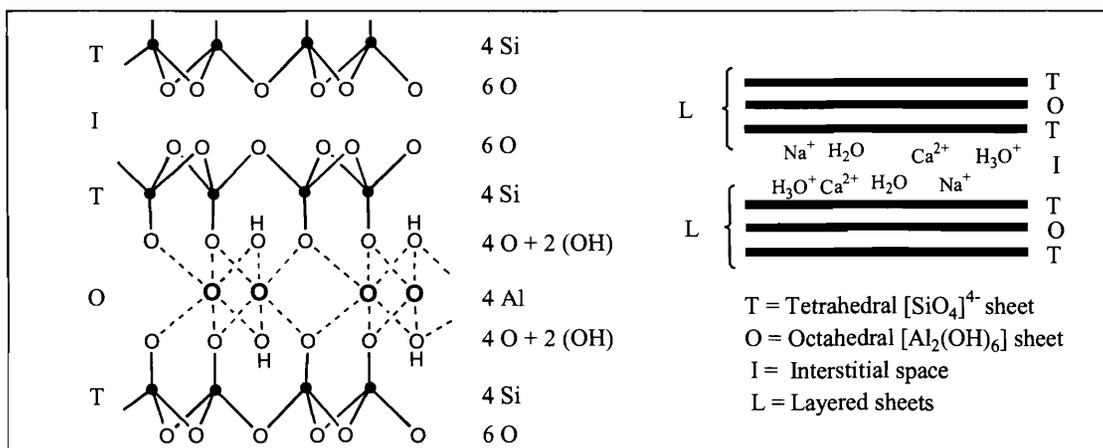
Clays are solid acidic catalysts which can function as both Bronsted and Lewis acids in their natural and ion-exchanged form. They are also known to act as radical catalysts. Modified smectite (swelling) clays can be very selective catalysts for a wide range of organic transformations. Using clay catalysts, environmentally benign green chemistry can be done both at industrial level and laboratory scale.

Clays are a class of soil with a particle size of <2 mm in diameter ($\sim 7.2 \times 10^{11}$ particles per gram of clay, which implies a surface area of about 23000 cm^2 per gram). Their characteristic physical features are, they are sticky and plastic when moist, but hard and cohesive when dry. Structurally, they are crystalline hydrous aluminosilicates, and also contain various other cations. Their chemical composition and crystal structure are the basis on which they are divided into four main groups such as, illite, smectite, vermiculite, and kaolinite. Among these, the one that is found to be most useful as a catalyst to the synthetic organic chemist is a subgroup of the smectite clay, called montmorillonite, which is the main constituent of bentonites and Fuller's earth.

The Structure and Properties of Montmorillonite Clay

The montmorillonite lattice is composed of a sheet of octahedrally coordinated gibbsite $[\text{Al}_2(\text{OH})_6]$ sandwiched between two sheets of tetrahedrally coordinated silicate $[\text{SiO}_4]^{4-}$ -sheets (Figure 1). The three-sheet layer repeats itself, and the interlayer space holds the key to the chemical and the physical properties of the clay (vide infra).

An important and useful property of montmorillonite stems from its high degree of efficiency for M^+ cation exchange. This happens because of charge imbalances in its structure caused by exchange of Al^{3+} for Si^{4+} in the tetrahedral sheets, and of Mg^{2+} for Al^{3+} cations in the octahedral sheets. The defects at the edges



of crystals also add to this imbalance. If approximately 20% of Al³⁺ positions are replaced by Mg²⁺, montmorillonite will gain a cation exchange capacity of 100 millimoles of M⁺ per 100 grams of clay. These balancing cations are presumably situated between the lattice layers. On wetting, the layers move apart by the entry of water molecules, thereby the clay swells and the existing interlayer cations become easily exchangeable. The catalytic properties of montmorillonite clay can be greatly manipulated to suit the needs of synthetic organic chemists. Chemically modified clays are considered to be potentially the most cost-effective nanomaterials, and it is estimated that hundreds of millions of dollars worth of clays will be marketed by 2010. A variety of organic reactions have been carried out with great success using such clays as catalysts. Some of these are very briefly described in this article to point out the importance of the efforts of chemists in utilizing clay catalysts for reducing environmental pollution.

The interlayer in montmorillonite clay normally contains Na⁺, Ca²⁺ and Mg²⁺ as compensatory cations for the charge imbalance. When the clay is dry these cations reside in the hexagonal cavities of the silica sheets. However, when it is treated with water, the cations relocate themselves in the interlamellar region and become exchangeable by a variety of both metallic and nonmetallic cations, for example, H₃O⁺, NH₄⁺, Al³⁺, Fe³⁺, R₄N⁺,

Figure 1. Structure of montmorillonite.

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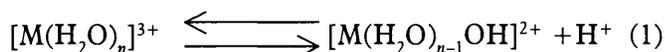
Higher levels of Bronsted acidity are achieved when highly polarizing ions such as Cr^{3+} have exchanged for Na^+ , Ca^{2+} , etc. present in the natural clay, and the water content is low.

R_4P^+ , etc. One of the most useful properties of clay minerals lies in this fact.

The Acidic Character of Clay

Organic reactions that take place under acid catalysis can be very efficiently carried out using clay catalysts, which may function as Bronsted or Lewis acids or both. The Lewis acidity is due to Al^{3+} and Fe^{3+} at the crystal edges, and can be further enhanced by exchange of the interlayer cations Na^+ and Ca^{2+} by Al^{3+} ions on treating the clay with AlCl_3 solution.

The Bronsted acid character of clays arises mainly due to the dissociation of the intercalated water molecules coordinated to cations (1). Higher levels of Bronsted acidity are achieved when highly polarizing ions such as Cr^{3+} have exchanged for Na^+ , Ca^{2+} , etc. present in the natural clay, and the water content is low. Besides the total acidity,



the surface area and the pore volume in the clay structure also add to the efficiency of the catalyst. Total acidity can be further increased by 'proton-exchange' on treating the clay with dilute acid or driving out NH_3 by heating the NH_4^+ ion treated clay. It is clear from this description that strong corrosive acid medium is completely avoided, if we use clay as Bronsted acid instead of mineral acids to achieve the same purpose.

A variety of organic reactions that are catalyzed by Bronsted acids such as H_2SO_4 , HCl , HNO_3 , AcOH , etc. or Lewis acids such as AlCl_3 , TiCl_4 , FeCl_3 , etc. have been shown to take place in clays, especially montmorillonite, more efficiently, i.e., under milder conditions, with greater selectivity, better yields, shorter reaction times and so on. Moreover, the work up and purification procedures are simpler as the catalyst is separated easily from the reaction mixture. Because of these reasons, and the fact that the catalyst can be reused or regenerated, the entire synthetic activity is not only economical but also environmentally benign.

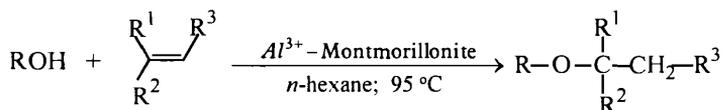
The range of reactions that have been successfully performed on clay catalysts includes addition, elimination, addition-elimination, substitution, rearrangement, Diels–Alder reactions, oxidation-reduction and others. It is not possible to give many examples, but an attempt is made to give a few representative reactions that would provide good and sufficient material to gain some insight into this area of organic synthesis.

Bronsted Acid Catalyzed Reactions

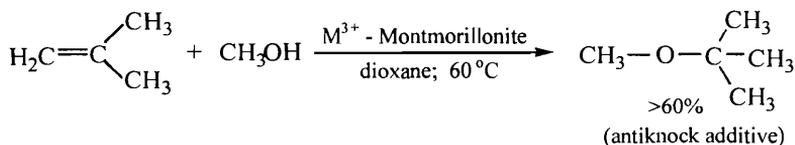
The first step of a reaction catalyzed by Bronsted acid is usually initiated by protonation of the reactant at the reaction site, which is either a double bond (unsaturated functional group) or a heteroatom with nonbonded electrons (usually oxygen, nitrogen or sulphur). The resulting cation then undergoes further transformation. Some examples are given below.

Ether formation

(a) Mixed or unsymmetrical ethers are efficiently prepared by refluxing a solution of alcohol and olefin in *n*-hexane using Al^{3+} -exchanged montmorillonite.

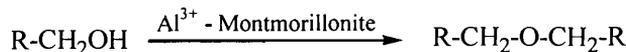


The yields are good in the case of primary alcohols. However, secondary alcohols give low yields, while tertiary alcohols do not give ethers, because dehydration occurs more easily. The olefin should be able to form a relatively stable carbocation intermediate, such as tertiary, benzylic or allylic. This ether forming reaction is far superior to the conventional Williamson's synthesis of such ethers.

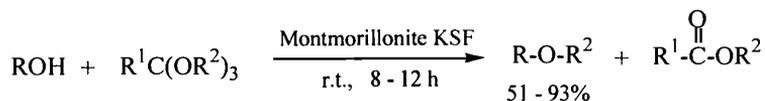


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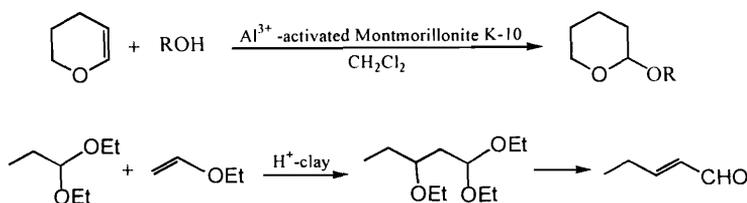
(b) By a similar process primary alcohols lead to symmetrical ethers.



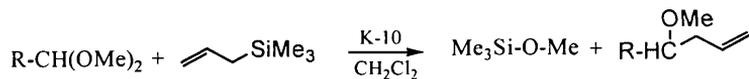
(c) Ethers have also been prepared efficiently by the reaction of primary alcohols with orthoesters.



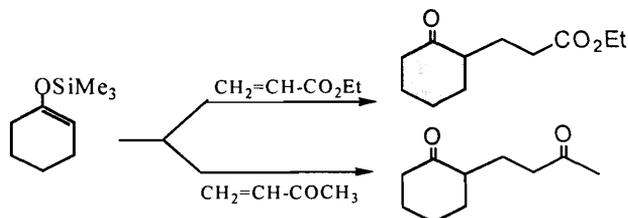
(d) Addition to enol ethers takes place smoothly in clay catalysts.



The acetal in the above equation, on treatment with formic acid-sodium formate, gives the α, β-unsaturated aldehyde, 2-pentenal. Acetals react with allyltrimethylsilane in presence of montmorillonite K-10 to give allylated ethers.



(e) Michael addition of silylenol ethers to α, β-unsaturated ketones and esters occurs in clay catalysts giving good yield of products.



Esterification

Conventional esterification methods usually involve the following reaction sequences.

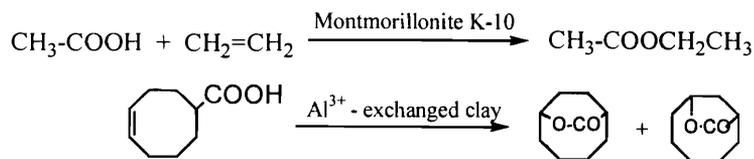
(1) Conversion of a carboxylic acid to its acid chloride followed by treatment of the latter with the desired alcohol in presence of a base, or

(2) Heating a mixture of the carboxylic acid and the alcohol in presence of a dehydrating agent such as conc H_2SO_4 , H_3PO_4 , silica gel, etc.

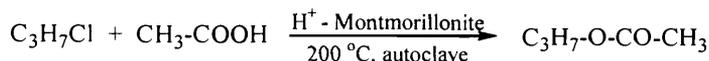
In most of these reactions the byproducts and the reactants such as SOCl_2 or PCl_5 used in the first method for the preparation of acid chlorides or the concentrated acids used in the second method are highly corrosive and extremely polluting. Avoiding these chemicals totally in synthesis is not only beneficial to the environment, but also cuts the cost of production considerably.

Three methods of clay-catalyzed ester-forming reactions are known.

(1) Addition of carboxylic acid to an olefinic compound leading to ester can be brought about in acid-activated montmorillonite clay as indicated below. The second compound is formed after isomerization of the double bond.

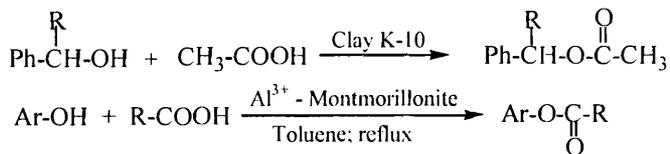


(2) Substitution of alkyl halide by carboxylic acid has been achieved by heating the reactants in presence of acidic clay in an autoclave.

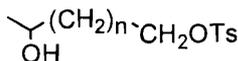
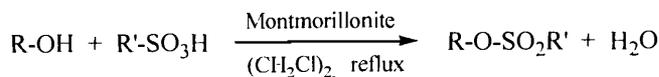


Diols can be selectively monotosylated.

(3) Refluxing mixture of alcohols or phenols with carboxylic acids with clay catalysts in solvents leads to esters.

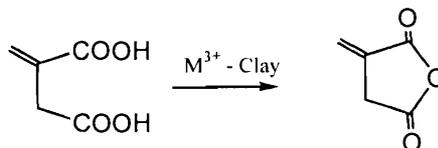
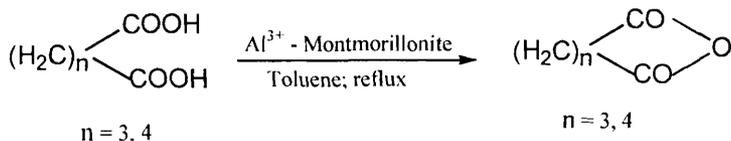


(4) In an analogous manner, tosyl or sulphonyl esters are prepared in good yields by refluxing alcohols with sulphonic acids using Fe^{3+} -montmorillonite in ethylene dichloride solvent. Diols can be selectively monotosylated.



Anhydride Formation

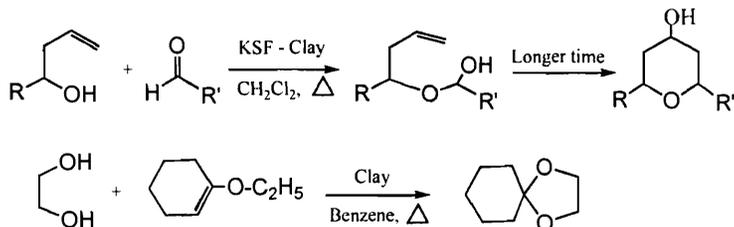
Another facile dehydration reaction occurring in acid clay medium is the formation of cyclic anhydrides from 5- and 6-carbon dicarboxylic acids. Note that the sensitive double bond in itaconic acid has not isomerized in the anhydride.



Reaction of Alcohols with Ketones and Aldehydes

Addition of alcohols to carbonyl compounds is found to occur

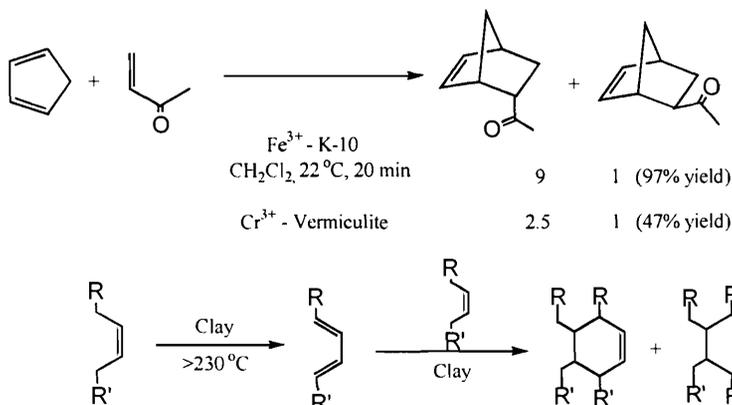
easily in the presence of montmorillonite clays. Acetals have been prepared by taking advantage of this fact. Recently, homoallyl alcohols have been observed to add to aldehydes leading to hemiacetal intermediates, which further undergo intramolecular transformation to give Prins-type cyclization products.



The endo:exo ratio can be manipulated by varying the exchanged cations, because the transition state geometry is controlled by the interlayer spacing.

Diels–Alder Addition

Though the Diels–Alder reaction is a thermally allowed [4+2] cycloaddition process, it does not occur spontaneously with all dienes and dienophiles. However, the rates of slow reactions are greatly accelerated when they are carried out using clay catalysts even under very mild conditions. Another important and useful finding in these reactions is that the endo:exo ratio can be manipulated by varying the exchanged cations, because the transition state geometry is controlled by the interlayer spacing. (Narrower spacing favours the exo isomer, as it is more compact than the endo isomer). The catalytic character of clays in these reactions is due to their Lewis acidity.



Isomerization of *n*-alkanes to branched chain alkanes in clay media is one of the most important processes in petrochemical industry.

An early Diels–Alder reaction carried out on an industrial scale was the dimerization of oleic acid on montmorillonite, and is schematically presented in the second equation above. (It is presumed that only the first step of dehydrogenation is clay-catalyzed, but not the Diels–Alder addition part itself).

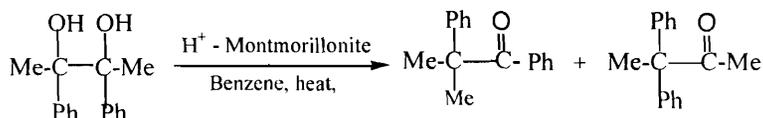
Rearrangement Reactions

A good number of rearrangement/isomerization reactions have been carried out using clay catalysts. Isomerization of *n*-alkanes to branched chain alkanes in clay media is one of the most important processes in petrochemical industry.

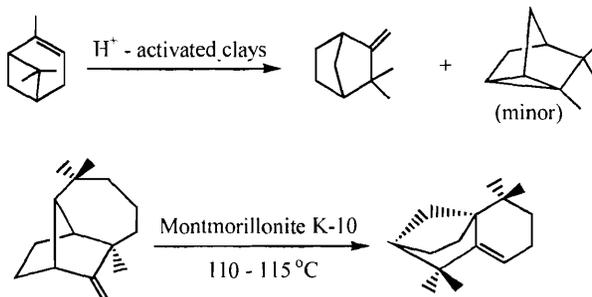
Clays having either the Bronsted acidity or the Lewis acidity can bring about desired rearrangement/isomerization under very mild conditions. Some examples follow.

1. Pinacol-pinacolone Reaction

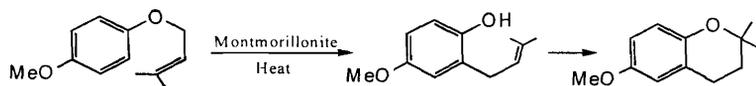
This is a common reaction of tertiary 1,2-glycols catalyzed by acids, in which an alkyl or an aryl group migrates to an adjacent position. Montmorillonite clay with Bronsted acidity is well suited for catalyzing such reactions, and excellent results have been achieved.



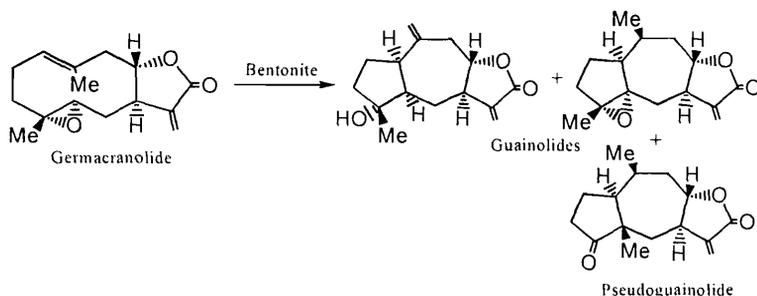
2. Isomerization of α -pinene to camphene and longifolene to isolongifolene has been carried out in good yields on acid-treated montmorillonite.



3. When aryl allyl ethers are heated on montmorillonite with Bronsted acidity, isomerization takes place with migration of the allyl group to the position ortho to the phenolic OH group. However, the products obtained are not of the Claisen rearrangement type. Longer reaction time finally gives benzopyran derivatives by the addition of H⁺ to the C=C bond.

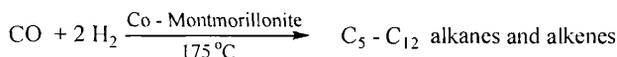
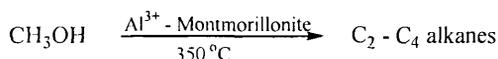
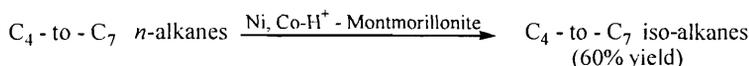


4. Transannular isomerization has been observed in germacranolide. It should be noted that the sensitive methylene lactone ring is not affected.



5. An important industrial application of clays can be found in petrochemical processing. Pillared clays¹ which are more stable at higher temperatures (>200 °C) are used in petroleum cracking, catalytic reforming and isomerization of *n*-alkanes to branched chain alkanes that increase the octane number. Conversion of methanol to alkanes and of synthesis-gas to hydrocarbons has also been achieved.

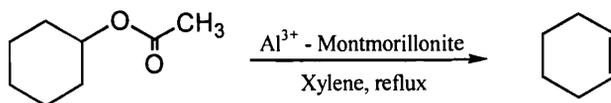
¹ Pillaring is a process by which clays are treated with certain inorganic or organic compounds that get into the interlayer space and prevent the collapse of the layers that would result due to removal of the interstitial water when clay is heated to >200 °C. Thus the reactant molecules enter the interlayer space and interact with the Lewis acid sites efficiently).



Clayfen and claycop are K-10 clay supported iron(III) nitrate and copper(II) nitrate reagents, respectively.

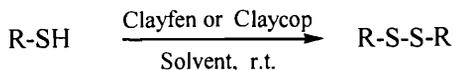
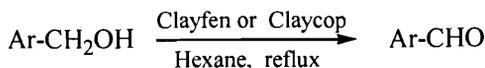
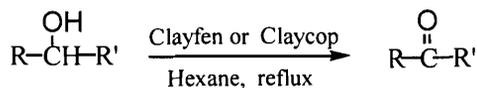
Pyrolytic Elimination

Esters on pyrolysis eliminate elements of acid to give olefins. These reactions require temperatures $>400\text{ }^{\circ}\text{C}$ in the absence of catalyst. However, using aluminum-exchanged montmorillonite, the same result can be achieved in refluxing xylene ($\sim 150\text{ }^{\circ}\text{C}$).



Oxidation-reduction Reactions

Clayfen and claycop are K-10 clay supported iron(III) nitrate and copper(II) nitrate reagents, respectively. Both are found to be excellent oxidizing reagents for alcohols, thio-compounds and many others.

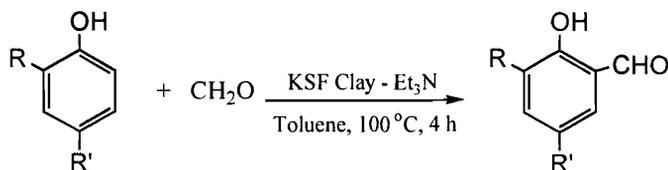


Suggested Reading

- [1] R W McCabe, Clay Chemistry, *Inorganic Materials*, D W Bruce and D O'Hare (Editors), John Wiley, New York, 1992.
- [2] M Balogh and P Laszlo, *Organic Chemistry Using Clays*, Springer, New York, 1993.
- [3] P T Anastas and T C Williamson, *Green Chemistry. Frontiers in Benign Chemical Syntheses and Processes*, Oxford University Press, Oxford, 1998.

Formylation of Phenols

Phenols have been formylated by reaction with formaldehyde using clay catalyst-controlled by R_3N . The introduction of the $-\text{CHO}$ group instead of the usual $-\text{CH}_2\text{OH}$ is also noteworthy here, which means there is an oxidation step at some stage.



Conclusion

The clay minerals can catalyze a variety of organic reactions occurring on their surface and interstitial space. Synthetic organic chemists have been attracted to their tremendous potential as catalysts only relatively recently. Modification of their properties by incorporating different metal cations, molecules or complexes, can lead to catalysts that are useful in effecting even more varieties of reactions and higher selectivity in product structure and yield. There is a theory that the molecules of life actually developed in sedimentary clays. As the organic chemist is becoming more aware of the clay's efficacy, its uses in organic synthesis are bound to increase, especially because it helps in developing eco-friendly chemical processes. The dark clay has a bright future in the area of organic synthesis.

Address for Correspondence

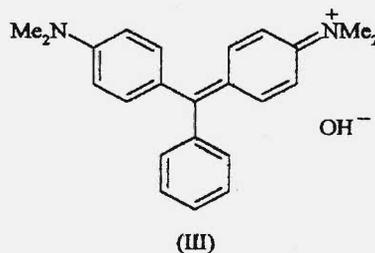
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Please Note: *Resonance*, Vol.6

Issue No.8

Page 91. The structure of the (III) shown in the article is incorrect. The correct structure is shown here.

Thanks are due to Dr S S Dua for pointing this out.



Issue No.10

Page 37. The name of the book in the first entry of the Suggested Reading should be '*e, The Story of a Number*'.

Issue No.11

Page 86. In the note on 'Logarithm and the agM', the constant in the formula for $L(a, b)$ should be π instead of 2 i.e., $L(a, b) = \pi \log\left(\frac{\sqrt{a} + \sqrt{b}}{2}\right)$. The reason is that the integral defining $L(a, b)$ is from 0 to $\pi/2$ and not from 0 to 1.

Thanks are due to Professor G V Anand of IISc for pointing this out.