



Review Article

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Montmorillonite: An efficient, heterogeneous and green catalyst for organic synthesis

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ABSTRACT

Reactions of organic molecules on Montmorillonite clay mineral have been investigated from various aspects. These include catalytic reactions for organic synthesis, chemical evolution, the mechanism of humus-formation, and environmental problems. Catalysis by clay minerals has attracted much interest recently, and many reports including the catalysis by synthetic or modified clays have been published. In this review, we will limit the review to organic reactions using Montmorillonite clay as catalyst.

Keywords: Montmorillonite, catalysis, clay, organic synthesis, green chemistry.

INTRODUCTION

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 [1].

In efforts aimed at the development of new drug compounds, pharmaceutical companies and academic research labs also generate a significant amount of chemical waste that is hazardous to the environment. Since the Pollution Prevention Act of 1990 was passed, however, chemists have attempted to minimize waste by designing new, more environmentally friendly methods for synthesizing useful organic compounds. This movement, often referred to as "Green Chemistry," has produced an array of improved methodologies, including the use of clays as chemical catalysts [2].

Natural aluminosilicates, such as zeolites and clays, are solid acids that are particularly promising candidates to substitute liquid acids in chemical transformations (Gates, 2003). Among these catalysts, natural and modified clays have attracted significant attention due to their extremely versatile properties (Balogh and Laszlo, 1993; Benesi and Winquest, 1978; Theng, 1974; Vaccari, 1999). The application of these catalysts are well-documented in organic synthesis, including in several recent reviews that summarize the current developments (Dasgupta and Török, 2008; Nikalje et al., 2000; Polshettiwar and Varma, 2008; Varma, 2002; Zhou, 2010). While many clay based catalysts such as claycopTM, clayzincTM, clayfenTM, envirocatTM, etc., are commercially available, the two most common

modified clays applied in organic synthesis are the K-10 and KSF montmorillonites. Both are synthetic clays produced from natural montmorillonites and are available from many suppliers in large quantities. While the physicochemical properties are similar their BET surface areas are quite different. K-10 has a higher surface area (about 250 m²g⁻¹) compared to that of KSF (10 m²g⁻¹) (Cativiela *et al.* 1993; Cseri *et al.*, 1995).

A catalyst is a chemical species that induces a chemical reaction to occur at a reasonable rate, without itself being consumed in the process; the catalyst can typically be recovered and reused. Development of naturally benign substances like clays as catalysts for chemical reactions constitutes an exciting breakthrough in Green Chemistry and promises to reduce the amount of hazardous waste associated with the synthesis of new compounds.

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. Application of naturally benign substances like Montmorillonite clays as catalysts for chemical reactions constitutes an exciting component of green chemistry [3].

In this review, we shall discuss the role of Montmorillonite clay mineral in catalyzing reactions of organic compounds, especially those reactions associated with acid catalysis. In particular, we shall describe our findings on the role of montmorillonite clay as a green catalyst in the organic reactions.

Basis of Clay catalysis:

“The synthetic chemist rarely borrows accessories for the laboratory from the vast stockroom of nature. We resist scooping some dust into a reaction flask. Yet elegant chemistry can be performed if clays are used as supports or catalysts.”

-Pierre Laszlo

An extensive study has been made of a wide range of organic reactions catalyzed by clay minerals (see, e.g., Fripiat and Cruz-Cumplido, 1974; Theng, 1974; Thomas *et al.*, 1977; Bittles *et al.*, 1964a, 1964b, 1964c). Recently, renewed interest has been shown in the use of natural and synthetic smectitic clays as highly selective acid catalysts (e.g., Adams *et al.*, 1978, 1979a, 1979b; Ballantine *et al.*, 1981a, 1981b).

Clay catalysts have been shown to contain both Brønsted and Lewis acid sites [4, 5] with the Bronsted sites mainly associated with the interlamellar region and the Lewis sites mainly associated with edge sites. The acidity of ion-exchanged clays is very much influenced by the quantity of water between the sheets. If the clay is heated (to around 100°C) so as to remove most of the interlamellar water until only 'one layer' of water remains, at about 5% total water level, the Brønsted acidity increases markedly [6, 7] to that of a very strong acid. Heating to a higher temperature (at around 200- 300°C) results in the collapse of the clay interlayer structure as the water is driven out, resulting in a decrease in Bronsted acidity but an increase in Lewis acidity. Further heating (to around 450°C and above) results eventually in complete dehydroxylation of the aluminosilicate lattice, producing a completely amorphous solid that retains Lewis acidity. Organic chemists, with synthesis in mind, have so far confined their interests to expandable montmorillonite clays [8, 9] and almost all of their clay catalysts have been either (a) acid-treated clays such as K-10 [10] or ion-exchanged clays such as Al³⁺, Cr³⁺ or H⁺ exchanged Wyoming or Texas bentonites [11]. The acid-treated and cation exchanged clays can be simply regarded as solid acids and act as heterogeneous catalysts, with all of the advantages of easy removal of the catalyst from the product. Acid-treated clays, because of their increased surface area and swelling properties, have also been widely used as solid supports for inorganic reagents such as potassium permanganate [12], thallium (III) nitrate [13]. The ion-exchanged clays have mostly Bronsted acidity in the interlamellar zone and so are characterised by promoting acid-catalysed reactions often of a bimolecular type between protonated and neighbouring unprotonated reactants [14].

Montmorillonite:

The chemical formula of montmorillonite (i.e. one kind of monoclinic) is Al₂Si₄O₁₀(OH)₂.nH₂O. Montmorillonite (MMT for short) may appear in variety of colors (e.g. yellow-green, yellow-white, gray and white) due to other trace metal elements; it typically forms microscopic or at least very small platy micaceous crystals. The moisture content is variable; in particular, due to swelling effects the volume of MMT crystal may increase several to thirty-fold after absorption of water. The crystalline structure of MMT consists of multiple layers and each layer made up of one octahedral alumina sheet sandwiched between two tetrahedral silica sheets [15].

Owing to approximately 0.9 to 1.2 nm of interlayer spacing and the excellent cation exchange property of MMT, MMT can form many nanocomposites with different organic compounds. Therefore, it expresses a significant capability to be used as a drug carrier for pharmaceutical purposes.

Montmorillonite clay's are layered silicates and are among the numerous inorganic supports for reagents used in organic synthesis. They can be used as an efficient and versatile catalyst for various organic reactions [16]. In Montmorillonite clay both Bronsted and Lewis acidic catalytic sites are available hence its natural occurrence as well as ion exchange properties allow it to function efficiently as a catalyst. The interlayer cations are exchangeable, thus allowing alteration of the acidic nature of the material by simple ion-exchange procedure [17]. In recent years Montmorillonite particularly Montmorillonite K-10 emerges as an efficient acidic catalyst in organic chemistry.

Montmorillonite as green catalyst:

The major current challenges before chemists are to develop synthetic methods that are less polluting, i.e., to design clean or 'green' chemical transformations. Clays are widely used due to its ecofriendly nature, these are non-toxic, non-corrosive, economical and recyclable, and thus are efficiently used for a variety of organic reactions [18].

Montmorillonite clays have been used as catalysts for number of organic reactions and offer several advantages over classical acids. For example the strong acidity, non-corrosive properties, cheapness, mild reaction conditions, high yields and selectivity and the ease of setting and working-up [19].

The reactions catalyzed by montmorillonite are usually carried out under mild conditions with high yields and high selectivities, and the workup of these reactions is very simple; only filtration to remove the catalyst and evaporation of the solvent are required. Montmorillonite catalysts are easily recovered and reused [20, 21].

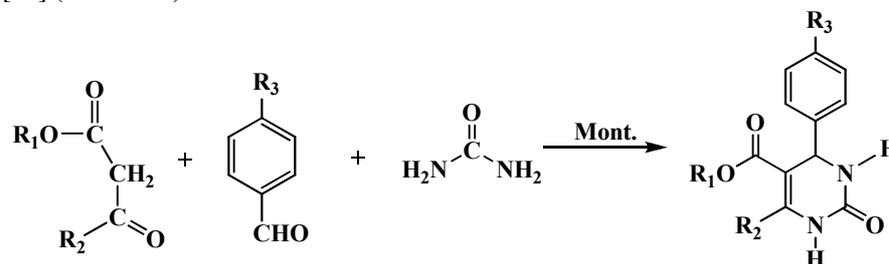
- Clays are: safe to handle, reusable, inexpensive, can prevent waste, promote atom economy
- May lower the activation energy of a reaction by stabilizing the transition state
- May act as a general acid or base
- Environmentally benign
- Use of clays as catalysts allows for them to be recycled, which further increases their economic efficiency.
- Furthermore, reactions that are catalyzed by clay are extremely easy to "work-up;" since the clay does not dissolve in the reaction medium (solvent), it must simply be filtered away when the reaction is complete.
- May provide a surface upon which reaction can occur

Montmorillonite: Role in organic synthesis

Montmorillonite clays are mined in regions all over the world and have been found to effectively catalyze a broad range of chemical reactions. Given their natural availability, low cost, and ease of use, however, application of clays in organic synthesis comprises an attractive topic for further investigation. The reaction proceeds efficiently in high yields at ambient pressure in a short time (two minutes) and without involvement of toxic and expensive material.

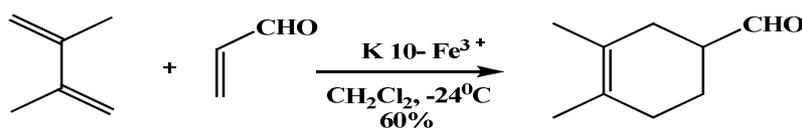
[1] Name reactions:

(a) **Biginelli reaction:** While optimizing the reaction conditions of the Biginelli reaction, it had been found that treatment of keto ester, aryl aldehyde and urea with KSF montmorillonite in methanol afforded DHPMs in good to excellent yields [22] (**Scheme-1**).

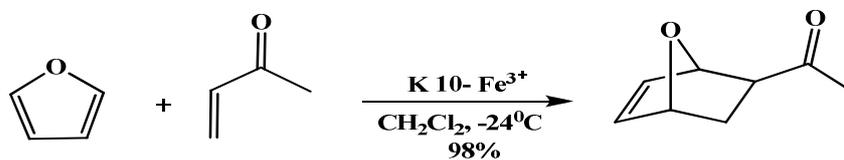


Scheme-1

(b) **Diels-Alder reaction:** Stereoselective Diels-Alder reactions involving an oxygen-containing dienophile are accelerated in the presence of Fe^{III}-doped montmorillonite in organic solvents [23]. Furans also undergo Diels-Alder reactions with acrolein and methyl vinyl ketone in CH₂Cl₂ to give corresponding cycloadducts in moderate yield [24]. The iron-doped clay also catalyzes the radical ion-initiated self-Diels-Alder cycloaddition of unactivated dienophiles such as 1,3-cyclohexadiene and 2,4-dimethyl-1,3-pentadiene [25] (**Scheme-2,3,4**).

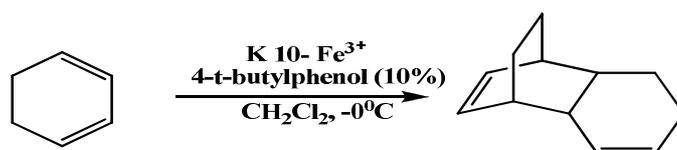


Scheme-2



Scheme-3

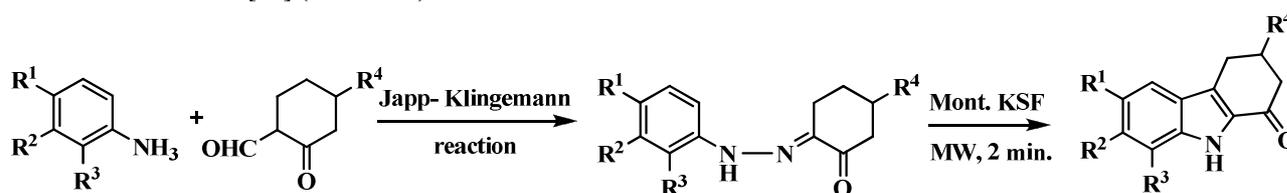
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Scheme-4

endo:exo=4:1

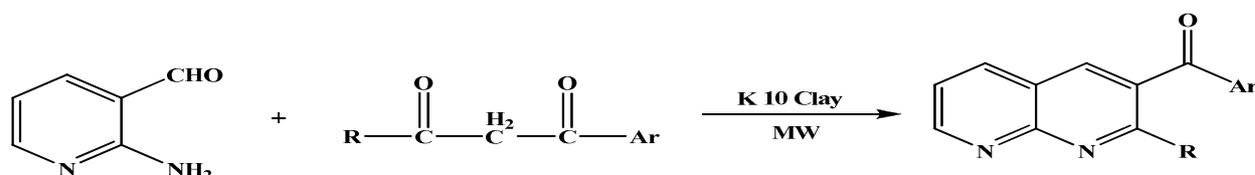
(c) **Fischer indole cyclisation:** Fischer indole cyclisation of substituted cyclohexane-1,2-dione-1-phenylhydrazones having either electron donating or electron withdrawing group on the phenyl moiety of substituted 1-keto-1,2,3,4-tetrahydrocarbazoles are efficiently carried out by microwave irradiation in presence of Montmorillonite-KSF under solvent free condition [26] (Scheme-5).



Scheme-5

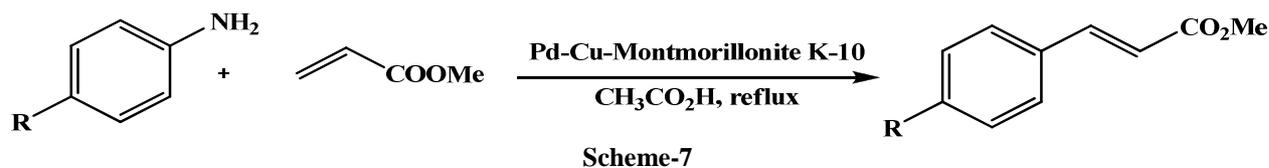
(d) **Friedel-Crafts acylation and alkylation:** The Friedel-Crafts acylation of aromatic substrates with various acyclic carboxylic acids in the presence of cation-exchanged (H^+ , Al^{3+} , Ni^{2+} , Zr^{2+} , Ce^{3+} , Cu^{2+} , La^{3+}) montmorillonites has been reported [27]. Curiously, the use of iron-doped montmorillonite was not included in the report; however, some catalysis is expected. Under these conditions, the yield of the desired ketones was found to be dependent on acid chain length and the nature of the interlayer cation.

(e) **Friedlander synthesis:** Friedlander condensation of 2-aminonicotinaldehyde on carbonyl compounds containing α -methylene is one of the most important preparation method of substituted 1,8-naphthyridines. The Friedlander condensation of 2-aminonicotinaldehyde with carbonyl compounds containing α -methylene in the presence of Montmorillonite K 10 clay in solvent free conditions under microwave irradiation afforded 1,8-naphthyridine derivatives [28] (Scheme-6).

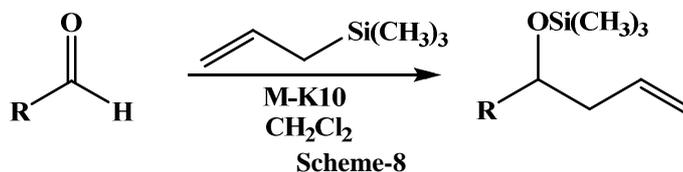


Scheme-6

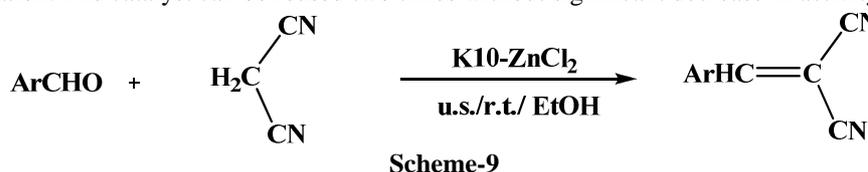
(f) **Heck vinylation:** Waterlot *et al.* reported direct synthesis of methyl cinnamates by Heck vinylation reaction of anilines with vinylacetate catalyzed palladium chloride and copper nitrate intercalated Montmorillonite K 10 as catalyst. The substituted methyl cinnamates were obtained in excellent yield without stilbene by product formation [29] (Scheme-7).



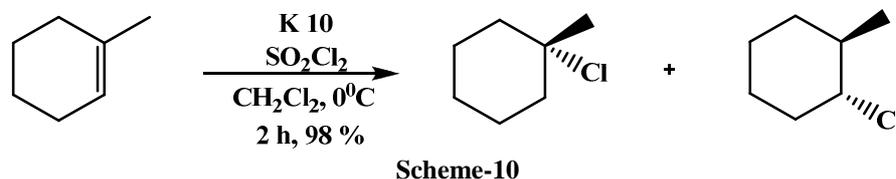
(g) **Hosomi-Sakurai (HS) Reaction:** It's a Lewis acid-catalyzed premiere C-C bond-forming reaction¹⁵. It occurs best with activated M-K10 and benzaldehydes by a concerted mechanism [30] (Scheme-8).



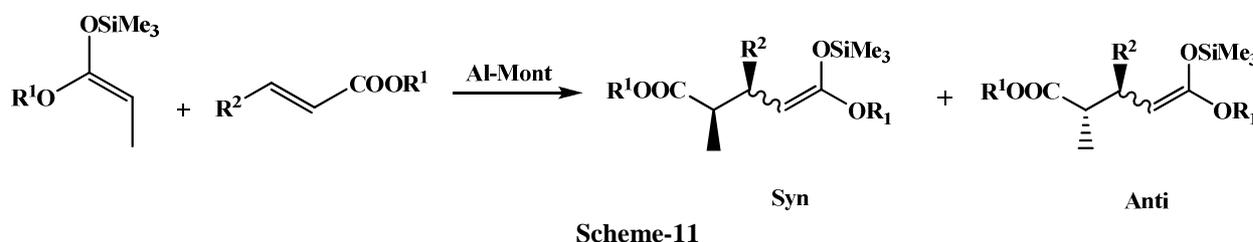
(h) **Knoevenagel condensation:** Knoevenagel condensation of malononitrile with aromatic aldehydes catalyzed by K 10–ZnCl₂ in anhydrous ethanol produces arylmethylenemalononitriles in 87–98% yield within 2–10 min under ultrasound irradiation. The catalyst can be reused two times without significant decrease in activity [31] (Scheme-9).



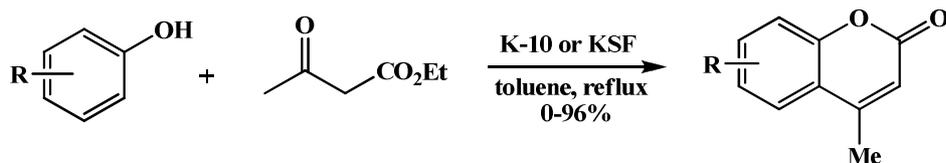
(i) **Markovnikov addition:** 1-chloro-1-methylcyclohexane, the Markovnikov adduct of hydrochloric acid and 1-methylcyclohexene becomes largely predominant when sulphuryl chloride is the chlorine source and K 10 the solid acid [32]. The reaction at 0°C, in dry methylene chloride, is complete within 2 h (Scheme-10).



(j) **Michael addition:** The Michael addition of an enolate to an α - β unsaturated carbonyl system is one of the most important reactions for carbon- carbon bond formation. Recently we have shown that clay monmorillonite is an efficient, heterogeneous acid catalyst for the aldol reaction of silyl enol ethers or silyl ketene acetals with aldehydes or acetals. The montmorillonite catalysed reaction has several prominent features : (1) Not only α - or β -monosubstituted acrylates but also α,β - or β,β -disubstituted acrylates are applicable. (2) The highly regioselective 1,4-addition to a polyenoate is achievable . (3) The Michael adduct can be obtained in the form of a labile silyl ketene acetal owing to a simple workup procedure [33] (Scheme-11).

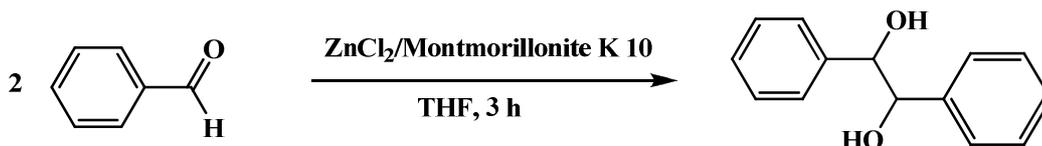


(k) **Pechmann Condensation:** Coumarins are synthesised *via* Pechmann condensation of phenols with ethyl acetoacetate catalysed by montmorillonite clay in satisfactory yields [34] (Scheme-12).



Scheme-12

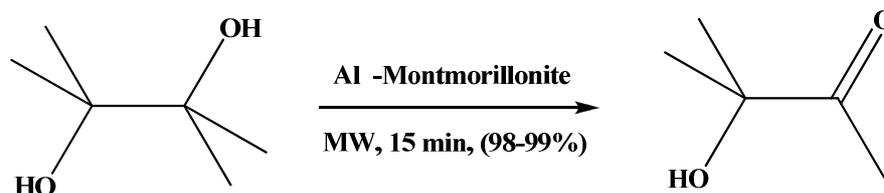
(1) **Pinacol coupling reaction:** A pinacol coupling reaction is an organic reaction in which a carbon-carbon covalent bond is formed between the carbonyl groups of an aldehyde or a ketone in presence of an electron donor in a free radical process. The reaction product is a vicinal diol. When reaction of benzaldehyde, Montmorillonite K-10 and zinc chloride in aqueous THF under ultrasound is carried out, the reaction time is reduced to 3 hours (composition 55:45) [35] (Scheme-13).



Scheme-13

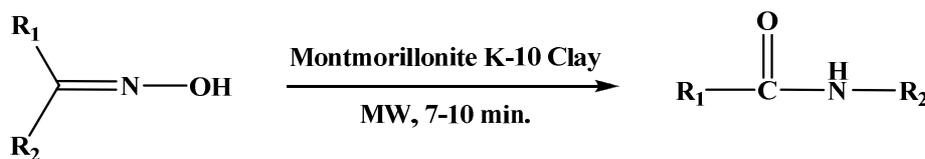
[2] **Rearrangement/Isomerization reactions:** A good number of rearrangement/isomerization reactions have been carried out using clay catalysts.

(a) **Pinacol–pinacolone rearrangement:** 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. Loupy and colleagues have reported a solventless pinacol–pinacolone rearrangement using microwave irradiation [36]. The process involves the irradiation of the *gem*-diols with Al^{3+} montmorillonite K 10 clay for 15 min to afford the rearrangement product in excellent yields (Scheme-14). These results are compared to conventional heating in an oil bath where the reaction times are too long (15 h).



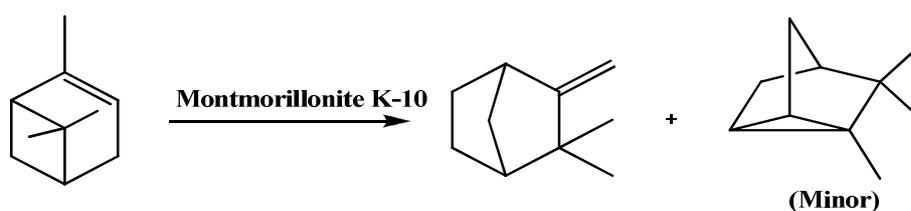
Scheme-14

(b) **Beckmann rearrangement:** Bosch *et al.* have achieved the Dehydration / Beckmann rearrangement of ketoximes with montmorillonite K 10 clay in 'dry' media in high overall yields [37] (Scheme -15).



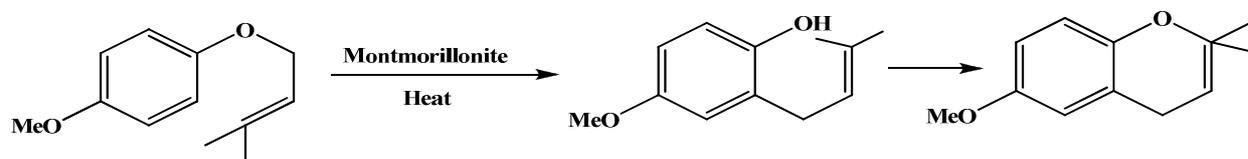
Scheme-15

(c) Isomerization of α -pinene to camphene and longifolene to isolongifolene has been carried out in good yields on acid-treated montmorillonite (Scheme-16).



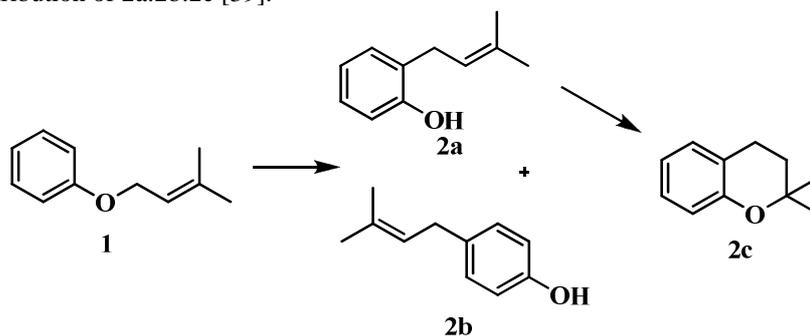
Scheme-16

(d) 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 (**Scheme-17**).



Scheme-17

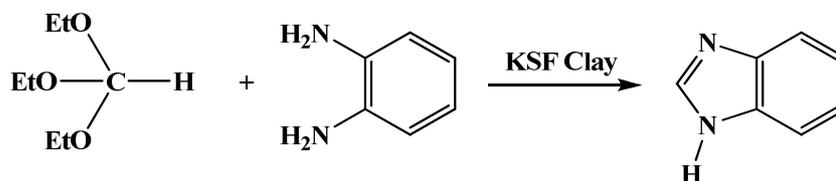
[3] **[1,3] shift reaction:** The Montmorillonite clay-catalyzed [1,3] shift reaction of allyl phenyl ether was originally reported by Dauben *et al.* in 1990 [38]. When Montmorillonite K10 clay is used a significant enhancement in the rate of conversion of **1** to **2a-c** is observed (**Scheme-18**). The starting material was completely consumed after 0.5 h, with a 1:0.7:0.1 distribution of 2a:2b:2c [39].



Scheme-18

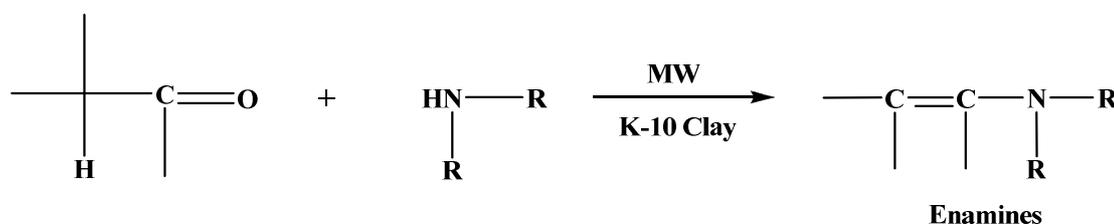
[4] Synthesis of heterocyclic compounds:

(a) **Benzimidazoles:** Benzimidazoles are prepared rapidly by condensation reaction of *ortho*-esters with *o*-phenylenediamines in the presence of KSF clay under either refluxing conditions in toluene or solvent-free conditions using focused microwave irradiation [40] (**Scheme-19**).



Scheme-19

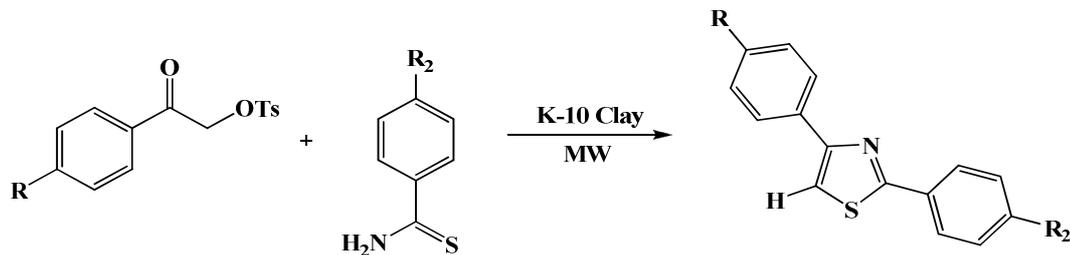
(b) **Isoflav-3-enes:** Isoflav-3-enes, possessing the chromene nucleus, are well known oestrogens and several derivatives of these oxygen heterocycles have attracted the attention of medicinal chemists. The results are especially promising in view of the convergent one-pot approach to the heterocyclic systems such as 2-substituted isoflavones wherein the generation of the enamine derivatives *in situ* and inducing subsequent reactions with *o*-hydroxyaldehydes in the same pot is the key feature [41] (**Scheme-20**).



R=morpholinyl or piperidinyl or pyrrolidinyl

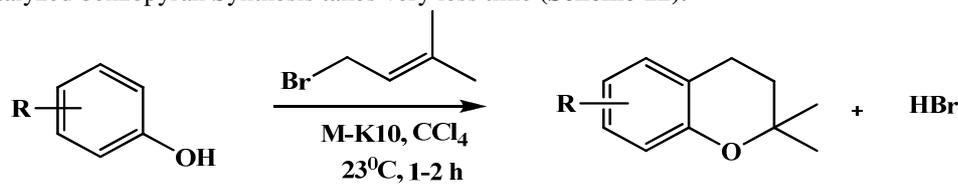
Scheme-20

(c) **Substituted thiazoles:** Thiazole and its derivatives are simply obtained by the reaction of a tosyloxyketones, which are generated *in situ* from arylmethyl ketones and [hydroxy(tosyloxy)iodo]benzene (HTIB) with thioamides in the presence of K 10 clay using microwave irradiation (**Scheme-21**) in a process that is solvent-free in both steps [42].



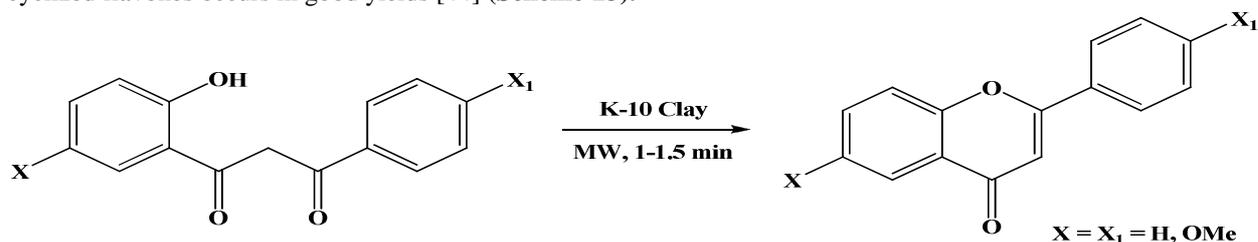
Scheme-21

(d) **Synthesis of Benzopyrans:** Benzopyran nucleus is common in natural products Coumarins and Flavanoids [43]. Clay-catalyzed benzopyran Synthesis takes very less time (**Scheme-22**).



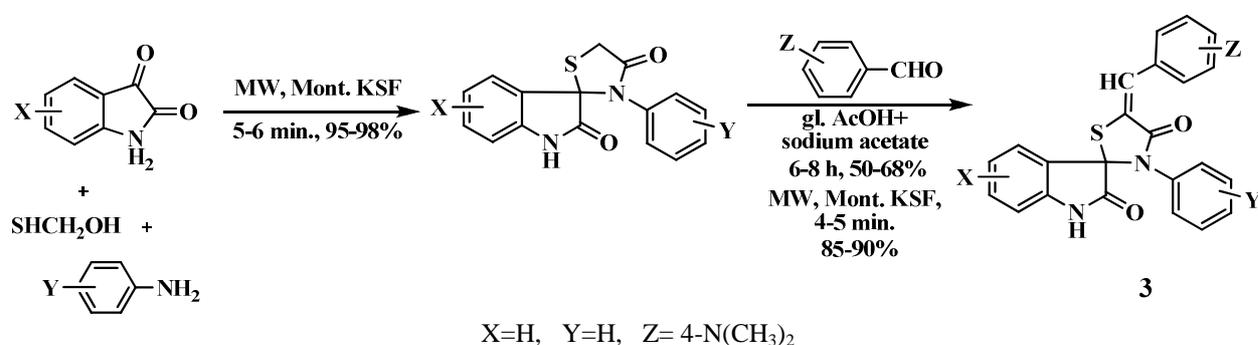
Scheme-22

(e) **Flavones:** Flavonoids are a class of naturally occurring phenolic compounds widely distributed in the plant kingdom, the most abundant being the flavones. Its synthesis simply involves the microwave irradiation of *o*-hydroxydibenzoylmethanes adsorbed on montmorillonite K 10 clay for 1–1.5 min. Rapid and exclusive formation of cyclized flavones occurs in good yields [44] (**Scheme-23**).

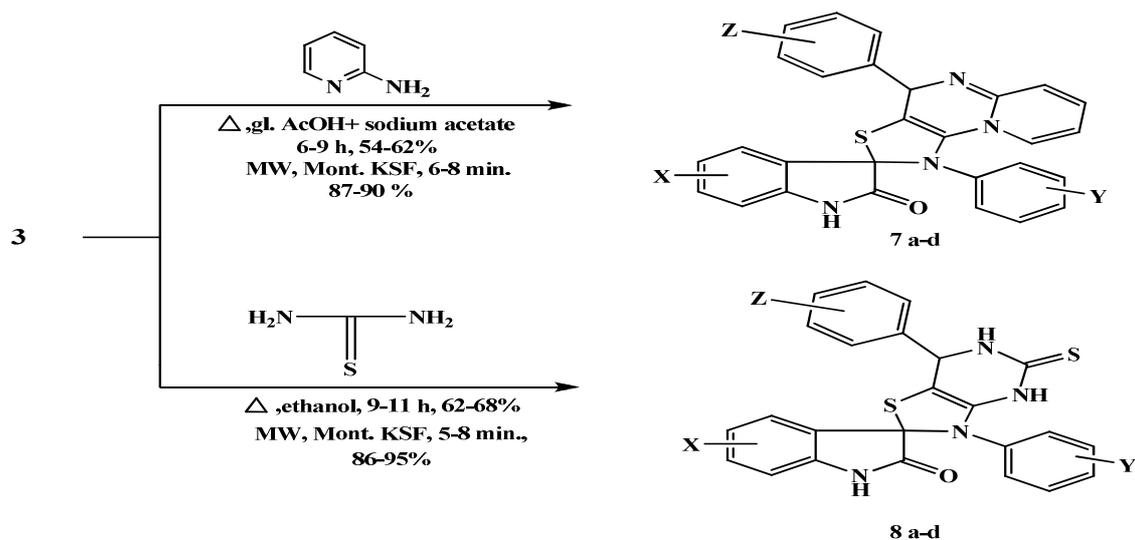


Scheme-23

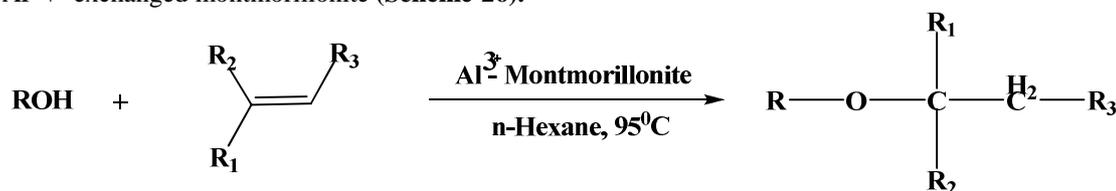
[5] **Synthesis of spiro heterocycles:** The arylidienes of spiro thiazolidines (**Scheme-24**) containing unsaturated function have been used as component of Micheal addition with equimolar amount of 2-aminopyridine to give novel spiro [indole-3, 2-pyrido-[1, 2-a]thiazolo[5,4-e]pyrimidines] in a single step under microwaves in presence of montmorillonite KSF as solid support. The new improved synthetic method for spiro [indole-3, 2-thiazolo-[4, 5-d]-pyrimidines] has also been developed involving the reaction of with thiourea under microwaves (**Scheme-25**). Comparison with conventional synthesis indicated the enhanced yield with faster reactions under microwaves [45].



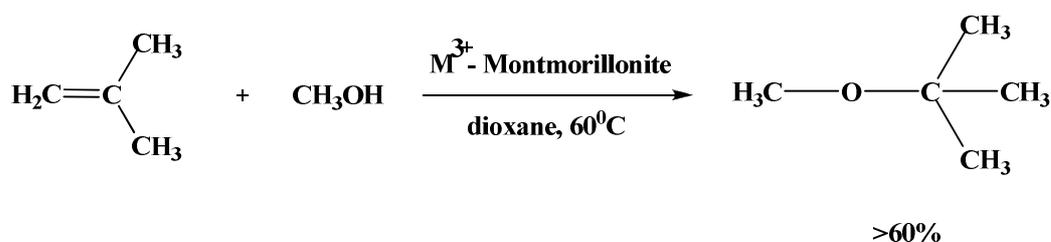
Scheme-24

**[6] Ether formation:**

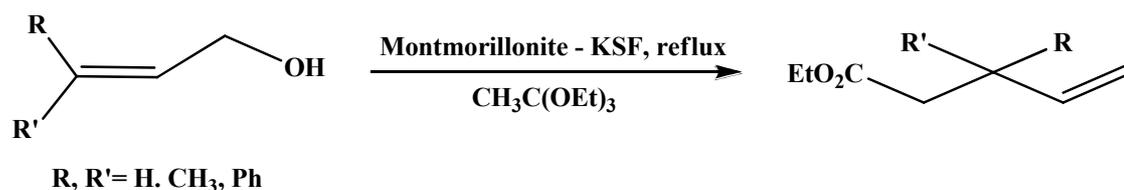
(a) Mixed or unsymmetrical ethers are efficiently prepared by refluxing a solution of alcohol and olefin in n-hexane using AP + -exchanged montmorillonite (**Scheme-26**).



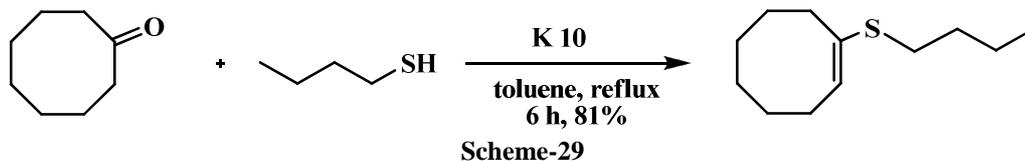
The yields are good in the case of primary alcohols. However, secondary alcohols give low yields, while tertiary alcohols do not give ethers, because dehydration occurs more easily. The olefin should be able to form a relatively stable carbocation intermediate, such as tertiary, benzylic or allylic. This ether forming reaction is far superior to the conventional Williamson's synthesis of such ethers.¹



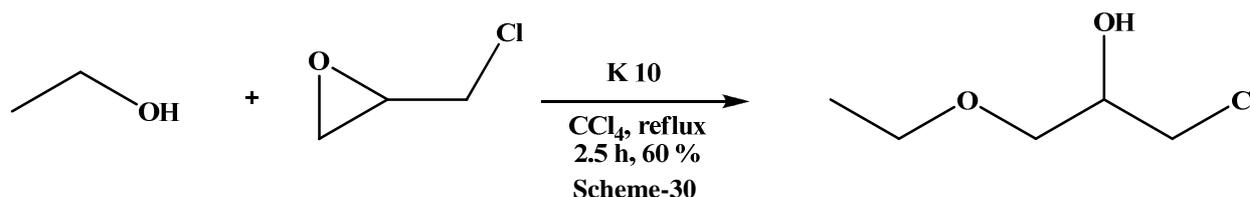
(b) Allylic and benzylic alcohols are converted into corresponding unsymmetrical ethers when reacted with various orthoesters in the presence of Montmorillonite KSF at ambient temperature [46] (**Scheme-28**).



(c) **Synthesis of Enol Thioethers:** Using a Dean -Stark water separator, K 10 catalyzes formation of alkyl and arylthioalkenes from cyclic ketones and thiols or thiophenoles, in refluxing toluene (**Scheme-29**). A similar catalysis is effected by KSF and K 10F [47]. The isomer distribution is under thermodynamic control.

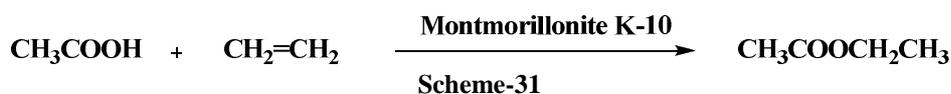


(d) **Preparation of monoethers of 3-chloro-1, 2-propanediol:** Alcohols react regioselectively with 1-chloro-2, 3-epoxypropane to form 1-alkoxy-2-hydroxy-3-chloropropanes. The K 10 catalysed process is carried out in refluxing carbon tetrachloride for 2.5 h [48] (**Scheme-30**). Yields are similar to those obtained by sulphuric acid catalysis.

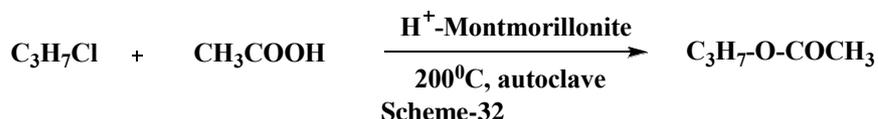


[7] **Acetalization:** ¹

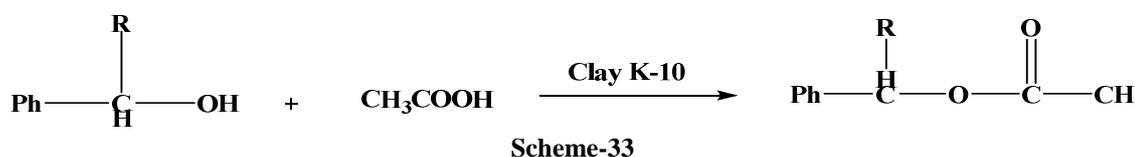
(a) Addition of carboxylic acid to an olefinic compound leading to ester can be brought about in acid-activated montmorillonite clay as indicated below. The second compound is formed after isomerization of the double bond (**Scheme-31**).



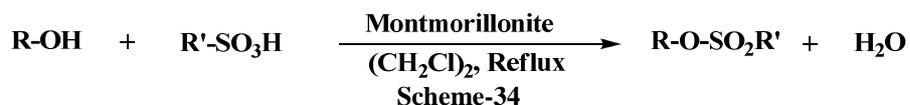
(b) Substitution of alkyl halide by carboxylic acid has been achieved by heating the reactants in presence of acidic clay in an autoclave (**Scheme-32**).

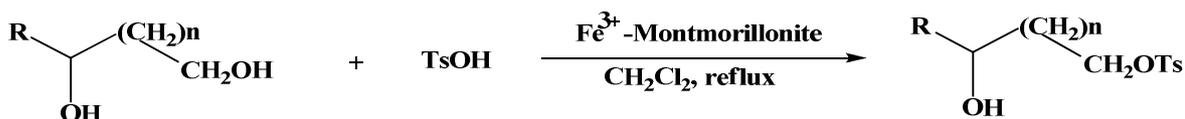


(c) Refluxing mixture of alcohols or phenols with carboxylic acids with clay catalysts in solvents leads to esters (**Scheme-33**).



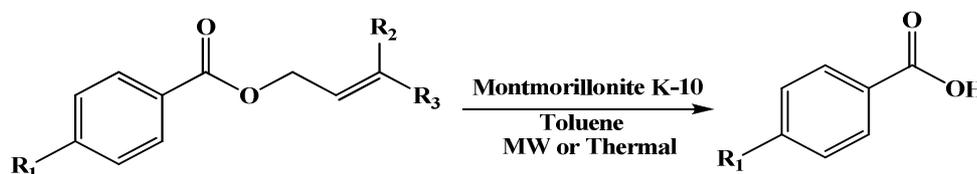
(d) In an analogous manner, tosyl or sulphonyl esters are prepared in good yields by refluxing alcohols with sulphonic acids using Fe³⁺-montmorillonite in ethylene dichloride solvent (**Scheme-34, 35**). Diols can be selectively monotosylated.





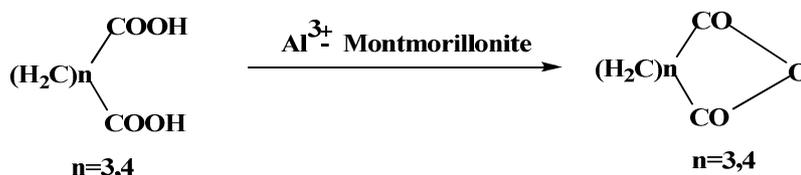
Scheme-35

[8] **Synthesis of carboxylic acids:** The allyl esters are selectively deprotected under mild and solvent free conditions to yield carboxylic acids in good yields (Scheme-35) with excellent chemoselectivity. The method provides almost 100 fold reduction of reaction time under microwave irradiation and reaction was performed under ecofriendly conditions [49].

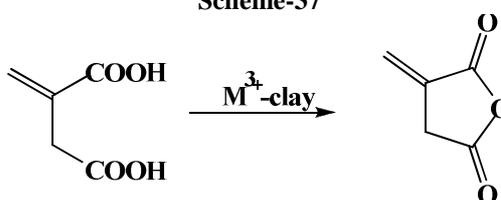


Scheme-36

[9] **Anhydride Formation:** Another facile dehydration reaction occurring in acid clay medium is the formation of cyclic anhydrides from 5- and 6-carbon dicarboxylic acids (Scheme-36, 37). Note that the sensitive double bond in itaconic acid has not isomerized in the anhydride.¹

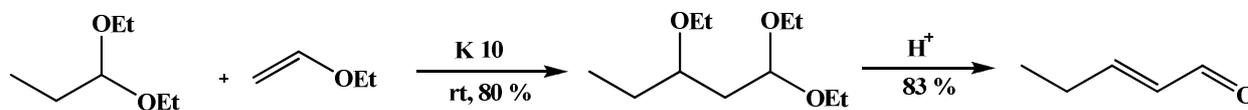


Scheme-37



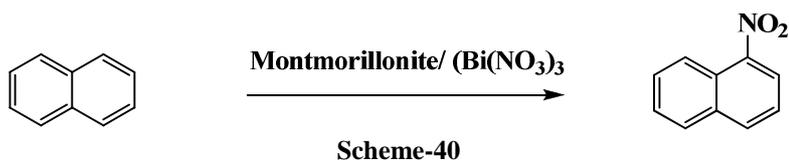
Scheme-38

[10] **Synthesis of α , β -Unsaturated aldehydes:** K 10 catalysed reaction of diethyl acetals with ethyl vinyl ether leads to 1, 1, 3-trialkoxyalkanes. Hydrolysis turns these into trans- α , β -Unsaturated aldehydes [50] (Scheme-38). The reaction is performed close to ambient temperatures. K 10 is superior to previously reported catalysts, such as boron trifluoride or iron (III) chloride. The addition is almost instantaneous and needs no solvent. Cyclohexanone diethyl acetal gives an analogous reaction.



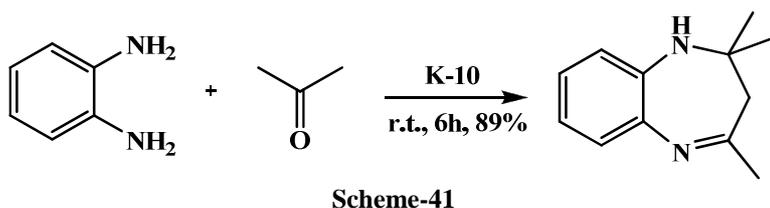
Scheme-39

[11] **Synthesis of Polyaromatic Nitro Compounds:** The nitration of aromatic compound shown in Scheme-39, naphthalene was regioselectively converted to the corresponding nitro compound by bismuth nitrate-montmorillonite in excellent yield. Interestingly, the site of the electrophilic attack by this reagent was found to be identical to the conventional nitric acid or acetyl nitrate mediated nitration reaction. Montmorillonite impregnated with bismuth nitrate has been found to be an excellent reagent for the synthesis of several nitro compounds of biological significance in high yield [51].

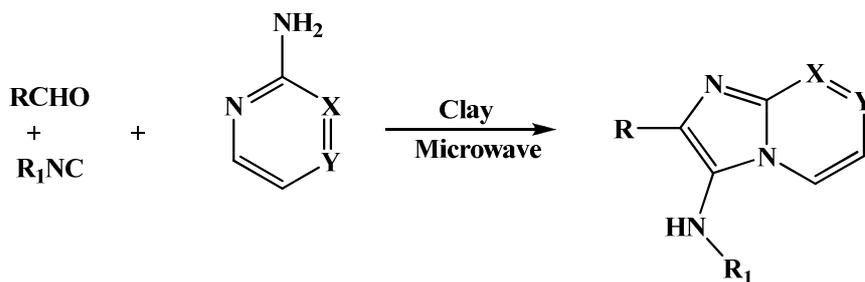


[12] Synthesis of biological active nuclei:

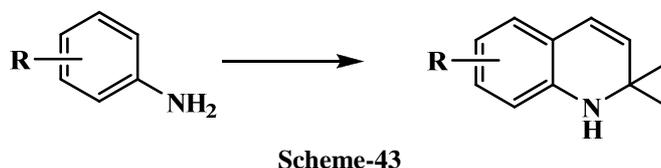
(a) Synthesis of 1, 5-Benzodiazepine Derivatives: 2, 3-Dihydro-1H-1,5-benzodiazepines have been synthesized under solventfree conditions in good yields from *o*-phenylenediamine and ketones catalyzed by montmorillonite K10 (**Scheme-40**). This method has advantages of mild reaction conditions, simple operation, and environmental friendliness [52].



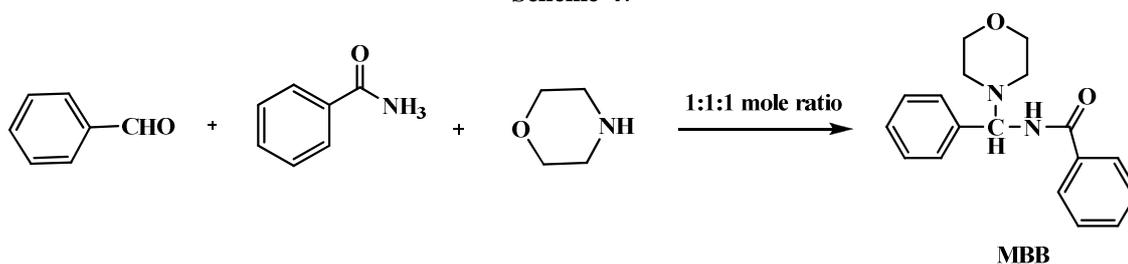
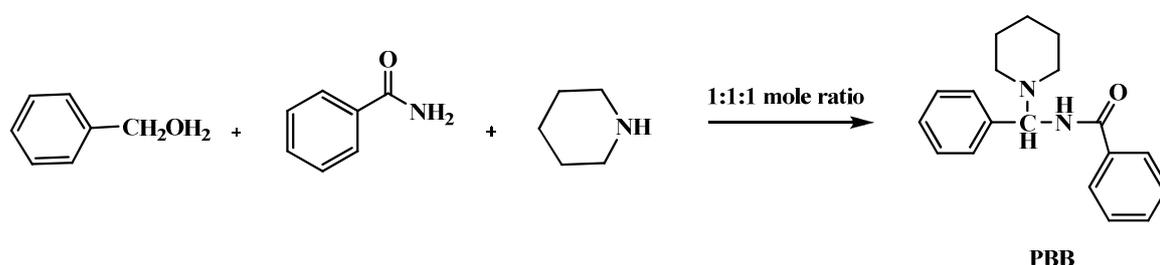
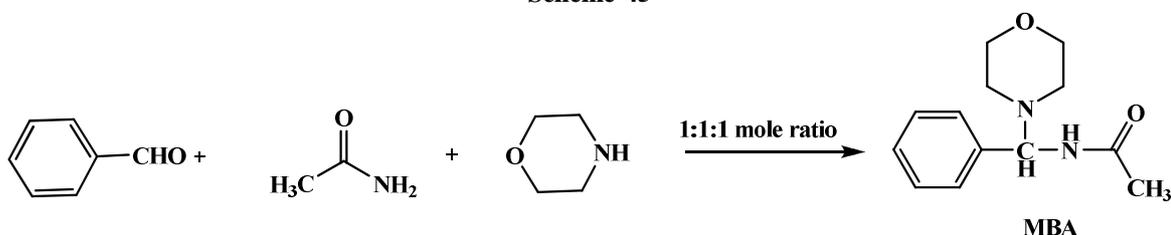
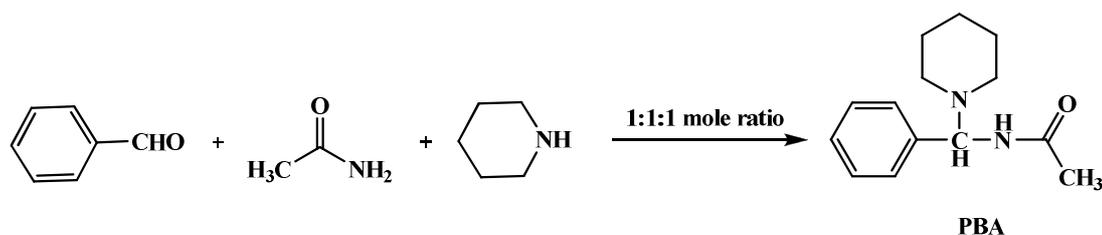
(b) Synthesis of Imidazole derivatives: Varma *et al.* reported one pot synthesis of imidazo [1,2-*a*] annulated pyrazines and pyrimidines via the condensation of aldehydes, amines and isocyanides catalyzed by Montmorillonite K 10 under microwave irradiation in solvent free conditions (**Scheme-41**).The method is an easy route for the synthesis of multisubstituted imidazo [1,2-*a*] pyridines, imidazo [1,2-*a*] pyrazines and imidazo [1,2-*a*] pyrimidines [53].



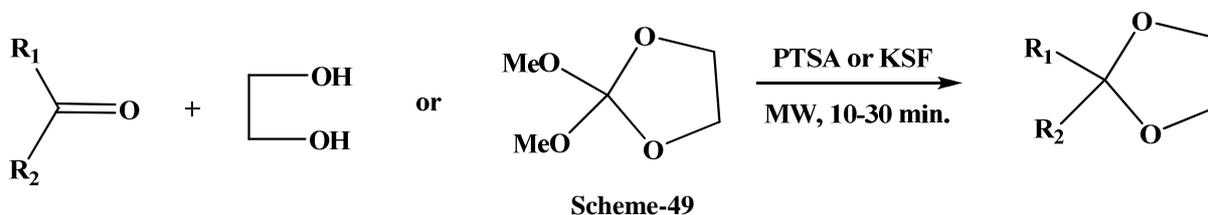
(c) Synthesis of quinolines: Treatment of a substituted aniline compound with prenyl bromide (an alkylating agent) in the presence of Montmorillonite K10 clay, results in successful generation of the corresponding quinoline product [54] (**Scheme-43**).



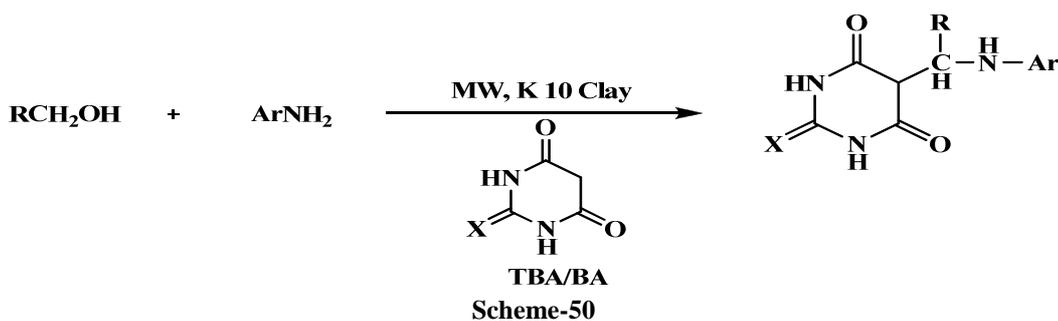
[13] Synthesis of Mannich bases: The synthesis of Mannich bases N-[1-(piperidinobenzyl) acetamide (**PBA**), N-[1-(morpholinobenzyl) acetamide (**MBA**), N-[1-(piperidinobenzyl) benzamide (**PBB**), N-[1-(morpholinobenzyl) benzamide (**MBB**) have been reported under microwave radiation catalysed by Montmorillonite K 10 clay (**Scheme-45-48**). The product is obtained in good yield [55].



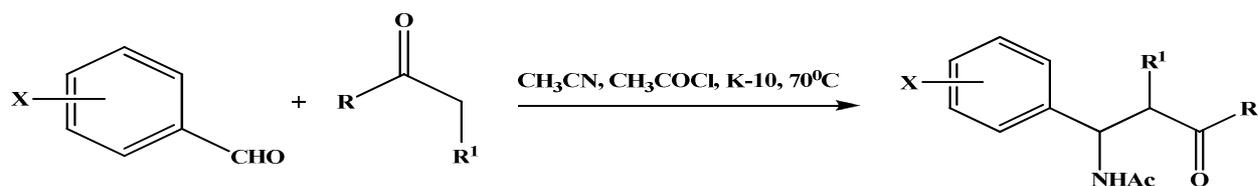
[14] **Formation of dioxolane:** Hamelin *et al.* have successfully protected aldehydes and ketones as acetals and dioxolanes using orthoformates, 1, 2-ethanedithiol or 2, 2-dimethyl-1, 3-dioxolane [56]. This acidcatalysed reaction proceeds in the presence of *p*-toluenesulfonic acid (PTSA) or KSF clay under solvent-free conditions (**Scheme-49**). The yields obtained with the microwave method are better than those obtained using the conventional heating mode (oil bath).



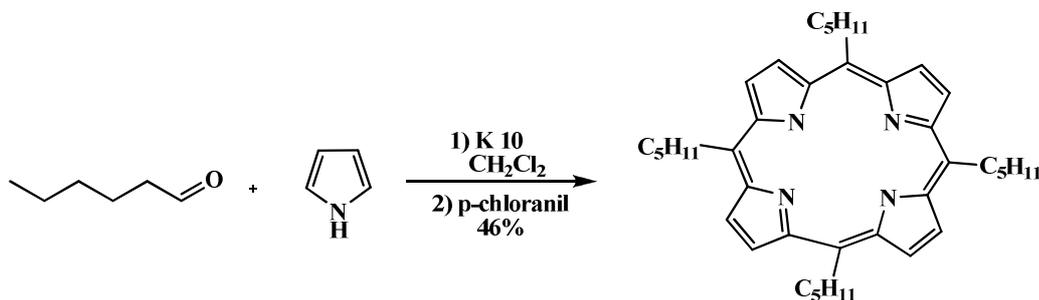
[15] **Synthesis of (Thio)Barbituric Acid:** In the view of the biological activity of thiobarbiturates, a facile, rapid, one pot synthesis of *N*-pyridyl/*N*-antipyryl-1-furyl/indolyl-1-[thiobarbituric acid/barbituric acid]aminomethane using montmorillonite clay in dry media under MWI (**Scheme-50**) [57].



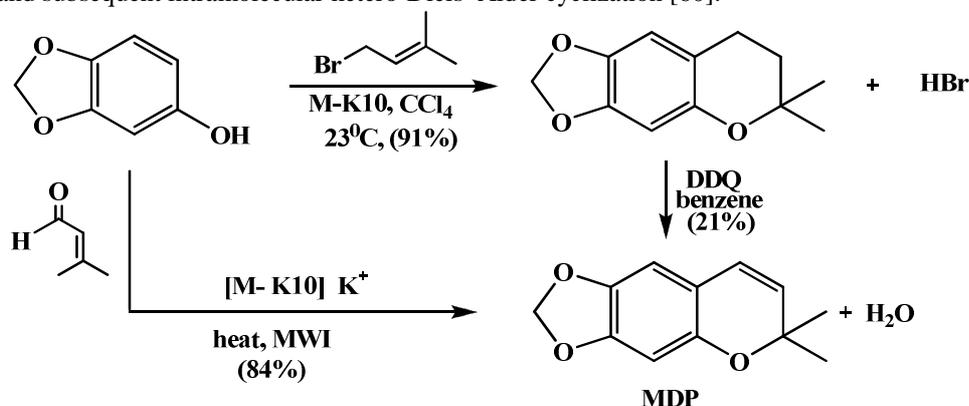
[16] **Synthesis of α -Acetamido Ketones:** Mont. K10- catalyzes three-component one-pot stereoselective synthesis of α -acetamido ketone following the protocol (**Scheme-51**). The isolation of these products was pretty much straightforward as the catalyst was removed by filtration and the filtrate was poured into ice-cold water, which resulted in precipitation of the desired α -acetamido ketones [58].



[17] **Porphyrin Synthesis :** Meso-tetraalkylporphyrins are formed in good yields from condensation of aliphatic aldehydes with pyrrole; thermally activated K 10 catalyzes the polymerization- cyclization to porphyrinogen, followed by p-Chloranil oxidation [59] (**Scheme-52**).



(18) **Methylenedioxyprococene (MDP):** The reported synthesis of MDP is conducted under solvent-free conditions, on basic Montmorillonite K10 clay, in a commercial microwave oven. The synthesis of MDP, outlined in (**Scheme-53**) involves electrophilic addition of 3-methyl-2-butenal to sesamol to give intermediate, followed by dehydration and subsequent intramolecular hetero-Diels–Alder cyclization [60].

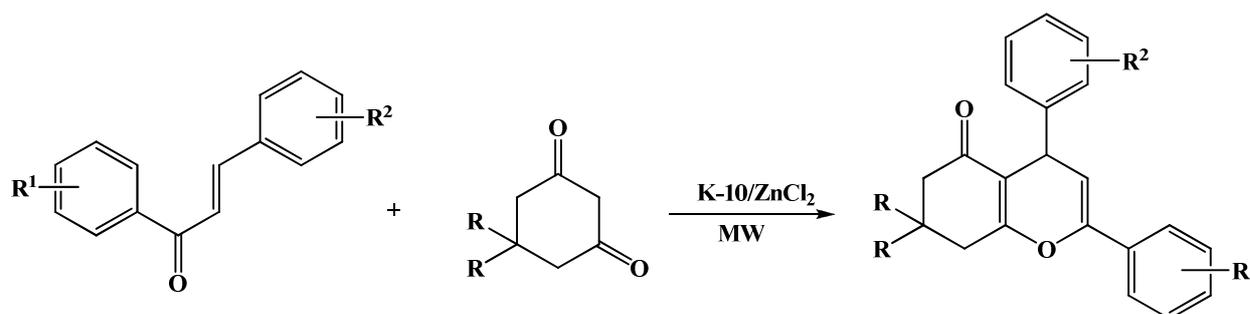


(19) Synthesis of γ -Lactones via the Ene reaction

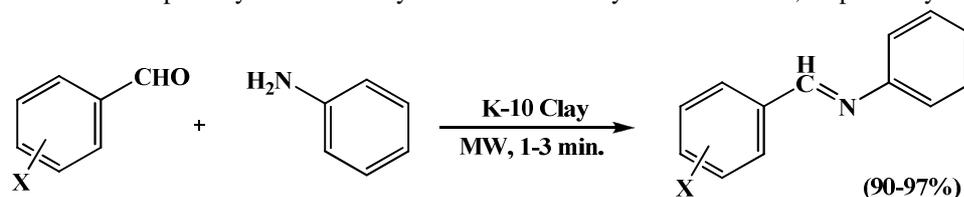
K 10 catalyzes the ene reaction of diethyl oximalonate and methyl-substituted alkenes at a rather low temperature for this reaction (80°C), followed by lactonization [61]. When alkene isomerization precedes the ene step, it results in a mixture of lactones. Using kaolinite instead of K 10 stops the reaction at the ene intermediate, before lactonization.

(20) Synthesis of 2, 4-Diphenyl-4*H*-chromen-5-one:

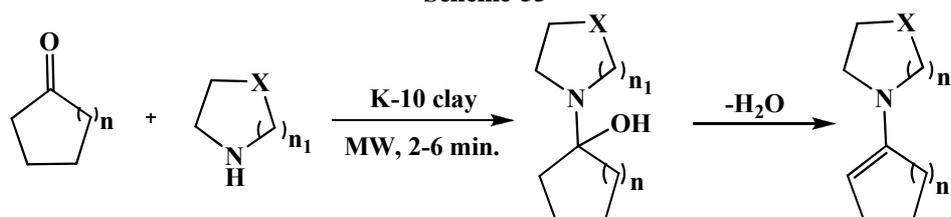
Tetrahydro chromen-5-one synthesis was achieved by microwave irradiations in the presence of ZnCl_2 /montmorillonite K 10 (**Scheme-54**). The corresponding 2, 4-diphenyl-4*H*-chromen-5-one forms in excellent yield [62].

**Scheme-54**

(21) Synthesis of imines and enamines: The driving force in the preparation of imines and enamines is the azeotropic removal of water from the intermediate, which is normally catalyzed by *p*-toluenesulfonic acid, titanium (IV) chloride, and montmorillonite K 10 clay. MW-induced acceleration of such dehydration reactions using montmorillonite K 10 clay [63] (**Scheme-55, 56**) has been demonstrated in a facile preparation of imines and enamines *via* the reactions of primary and secondary amines with aldehydes and ketones, respectively.



X=H, *o*-OH, *p*-OH, *p*-Me, *p*-OMe, *p*-NMe₂

Scheme-55

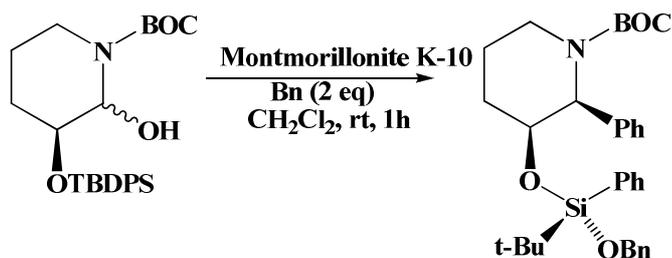
$n=1$; $n_1=2$; X= CH₂ ; $n=1$; $n_1=2$; X= O

$n=2$; $n_1=1$; X= CH₂ ; $n=2$; $n_1=2$; X= CH₂

$n=2$; $n_1=2$; X= O

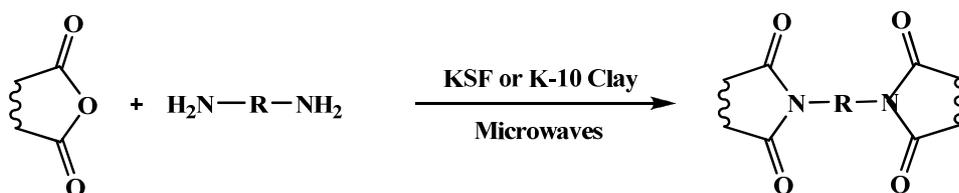
Scheme-56

(22) Asymmetric synthesis of arylhydrocyclic amines and silanols: Montmorillonite K 10 is utilized in a novel aryl migration from silicon to carbon which forms an efficient approach to the asymmetric synthesis of arylhydrocyclic amines and silanols [64] (**Scheme-57**).



Scheme-57

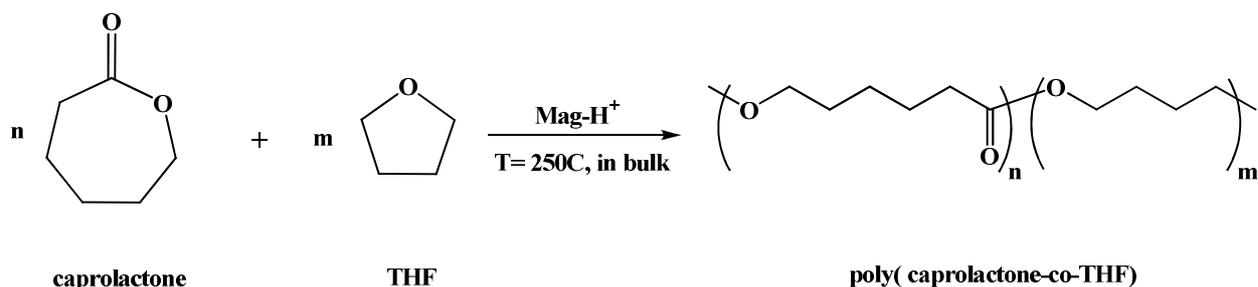
(23) **Synthesis of bismaleimides and bisphthalimides:** Different bismaleimides and bisphthalimides were synthesized in a simple and environmentally benign method from the condensation reaction of maleic and phthalic anhydrides with different diamines on montmorillonite KSF and montmorillonite K-10 clays as solid acidic catalysts by microwave [65] (Scheme-58).



Scheme-58

(24) **Synthesis of poly-(ϵ -caprolactone-co-tetrahydrofuran):**

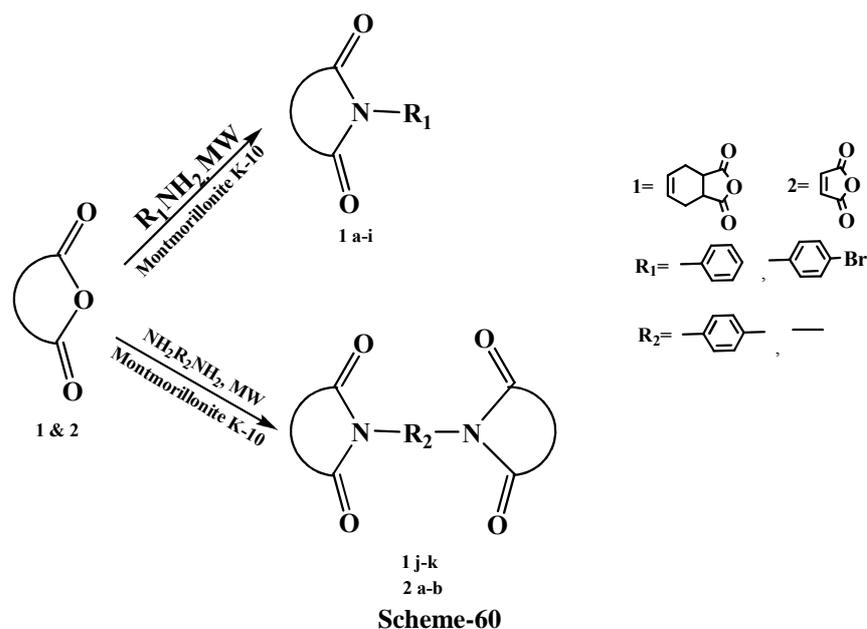
Maghnite- H^+ proton exchanged montmorillonite clay is effective as an acidic catalyst for the copolymerization of ϵ -caprolactone with THF [66] (Scheme-59).



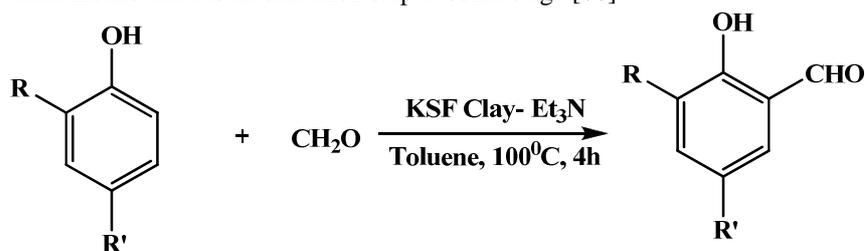
Scheme-59

(25) **One-pot synthesis of symmetric diimides and 3a, 4, 7, 7a-tetrahydroisindole-1,3-dione:**

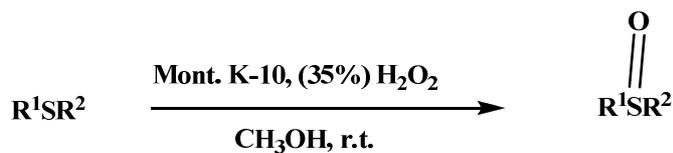
Montmorillonite K-10 clay has been used as an efficient catalyst for the formation of cyclic imides and diimides. The syntheses of *cis*-3a,4,7,7a-tetrahydroisindole-1,3-dione derivatives and some cyclic diimides were performed by the reaction of different aromatic and aliphatic amines and diamines with *cis*-1,2,3,6-tetrahydrophthalic anhydride and maleic anhydride on montmorillonite K-10 under microwave irradiation and solvent-free conditions [67] (Scheme-60).



(26) Formylation of Phenols: Phenols have been formylated by reaction with formaldehyde using clay catalyst-controlled by R_3N (Scheme-61). The introduction of the $-CHO$ group instead of the usual $-CH_2OH$ is also noteworthy here, which means there is an oxidation step at some stage [68].



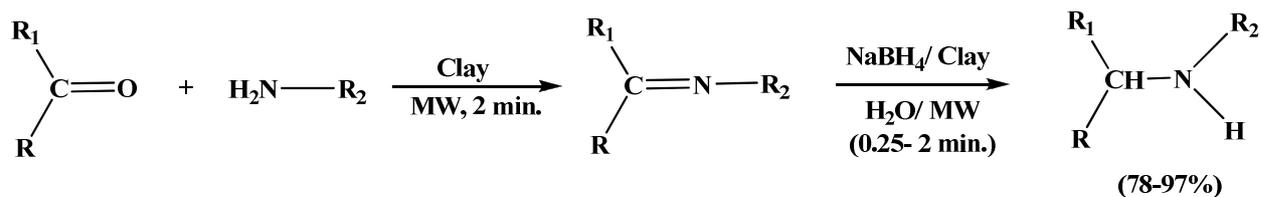
(27) Oxidation of Sulfides to Sulfoxides: A series of structurally different sulfides were oxidized selectively at room temperature in excellent yields. This reaction is very simple and proceeds without over-oxidation under mild condition, and shows many advantages over the existing methodologies. Using this procedure, sulfides bearing functional groups such as hydroxyl, methoxy, amino, nitrile, aldehyde, and olefinic double bond remained intact. The complete conversion was accomplished in the presence of small amounts of Montmorillonite K10 within 2.5 hours [69] (Scheme-62).



$R^1, R^2 = \text{alkyl, aryl, allyl}$

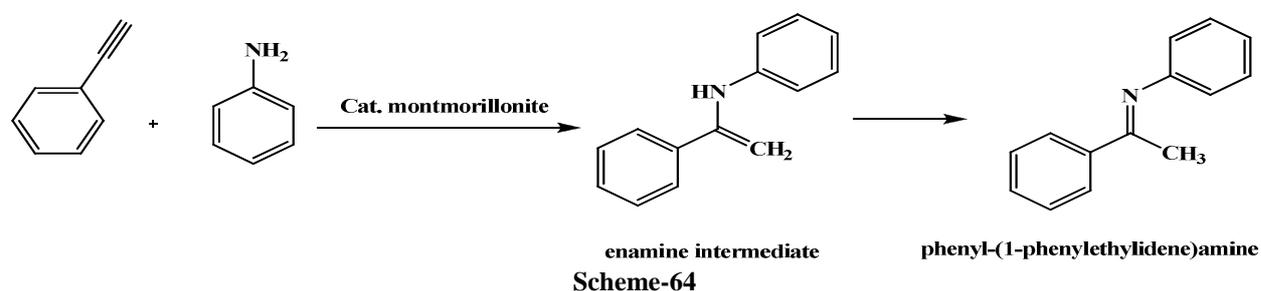
Scheme-62

(28) Reductive alkylation of amines: The studies pertaining to the solid state reductive amination of carbonyl compounds on various inorganic solid supports such as alumina, clay, silica, *etc.*, and especially on K 10 clay surface deliver secondary and tertiary amines rapidly [70] (Scheme-63). Clay not only behaves as a Lewis acid but provides water from its interlayers that enhance the reducing ability of $NaBH_4$.

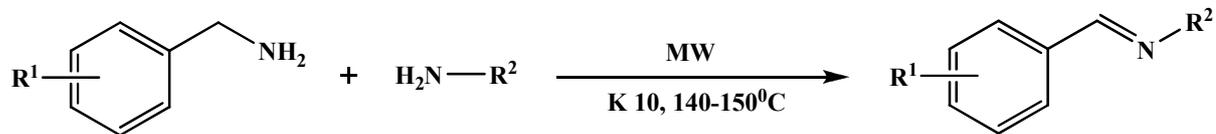


$R = i\text{-Pr, Ph, } o\text{-HOC}_6\text{H}_4, p\text{-MeOC}_6\text{H}_4, p\text{-NO}_2\text{C}_6\text{H}_4; R_1 = \text{H}; R_2 = \text{Ph}$
Scheme-63

(29) **Hydroamination of alkynes:** Intermolecular hydroamination of phenyl acetylene by aniline to give phenyl-(1-phenylethylidene) amine (Scheme-64) was chosen as a model reaction for testing the performance of metal exchanged K-10 as a catalyst. In the above reaction, enamine is formed as an intermediate, which being unstable undergoes rearrangement to form stable phenyl-(1-phenylethylidene) amine. This reaction is highly regioselective and only Markovnicov addition product was formed under the reaction conditions studied [71].



(30) **Coupling of amines to imines:** It was pointed out that benzylamines could react with these amines to produce mixed benzylideneamines (Scheme-65). The reactions provided the products in good yield (Scheme 1) [72].

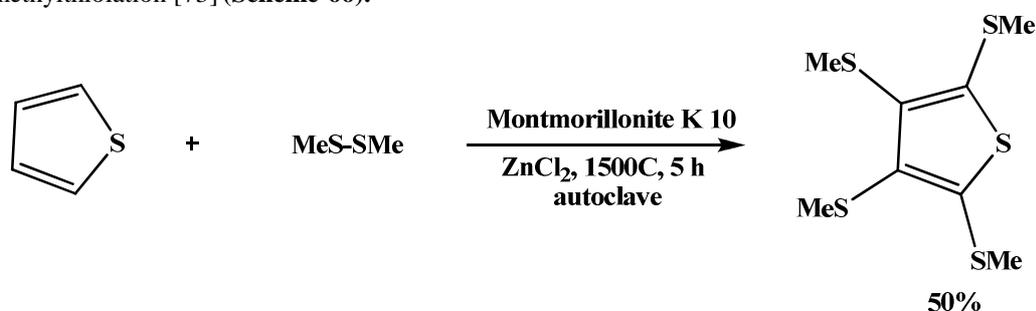


$R^1 = 3\text{-CH}_3, 4\text{-CH}_3, 2\text{-F}, 4\text{-F}, 4\text{-Cl}, 3\text{-CF}_3, 2\text{-OCH}_3$

$R^2 = \text{substituted benzyl, alkyl, aryl}$

Scheme-65

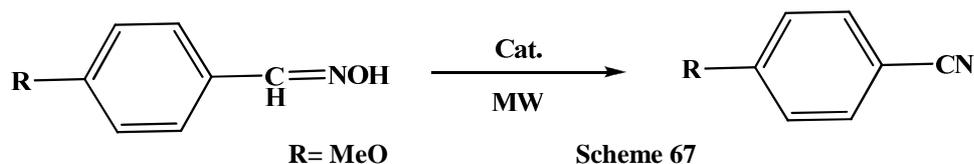
(31) **Methylthiolation of thiophenes:** When autoclaved with ZnCl_2 -doped-montmorillonite K10, thiophene undergoes pemethylthiolation [73] (Scheme-66).



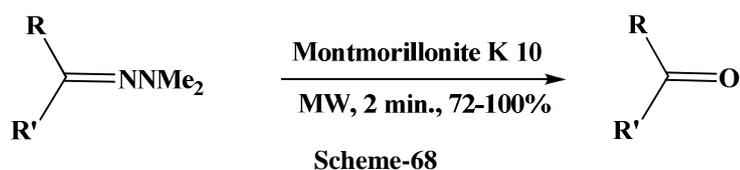
Scheme-66

(32) **Conversion of aldehydes into the nitriles:** The conversion of aldehydes into the corresponding nitriles is an important organic transformation. Multistep and one-pot conversion of aldehydes to nitriles were carried out conveniently without solvent using $\text{KF/Al}_2\text{O}_3$, montmorillonite KSF and K10 as catalyst, under microwave

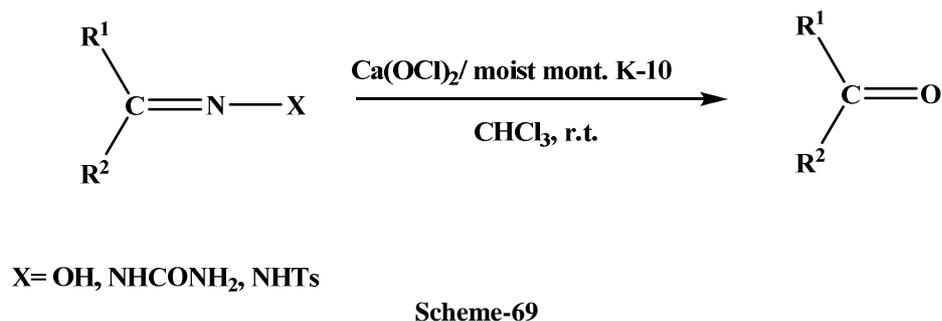
irradiation (**Scheme-67**). The reactions are completed within 6-8 min to give satisfactory yields. $\text{KF}/\text{Al}_2\text{O}_3$ was more effective catalyst both in multistep procedure and one-pot reaction [74].



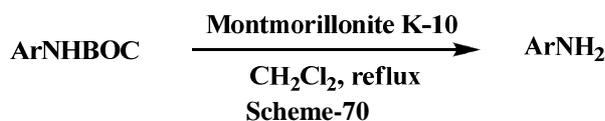
(33) Deprotection of Ketone Dimethylhydrazones: *N,N*-Dimethylhydrazones of ketones were efficiently and rapidly deprotected to the corresponding ketones by Montmorillonite K-10 clay using microwave irradiation under solvent free conditions. For example, when acetophenone dimethylhydrazone was treated with montmorillonite K-10 under microwave irradiation acetophenone was obtained in quantitative yield [75] (**Scheme-68**).



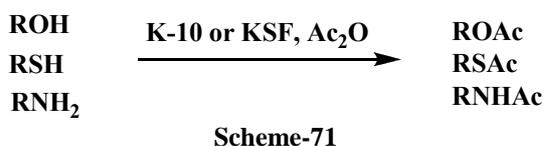
(34) Regeneration of carbonyl compounds from oximes, semicarbazones and tosylhydrazones: Oximes, semicarbazones and tosylhydrazones are converted into the corresponding carbonyl compounds in the presence of calcium hypochlorite and moist montmorillonite K-10 under mild and heterogeneous conditions [76] (**Scheme-69**).



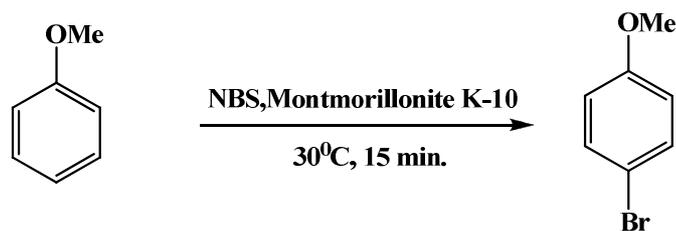
(35) Deprotection of N-BOC group: Montmorillonite K-10 is used as catalyst for the selective deprotection of N-BOC group. The N-BOC group of aromatic amines selectively deprotected without effecting the aliphatic N-BOC protected amines [77] (**Scheme-70**).



(36) Acylation: Montmorillonite K-10 and KSF are highly efficient catalysts for the acylation of a variety of alcohols, thiols, phenols and amines with acetic anhydride. No selectivity is observed between primary and secondary hydroxy groups in the presence of K-10 and KSF. The catalysts are found not to be efficient for acylation of tertiary alcohols. The catalysts are also effective for the acylation of alcohols, thiols, phenols and amines (**Scheme-71**) with acetyl chloride and benzoyl chloride. Cyclic anhydrides such as succinic anhydride, maleic anhydride and phthalic anhydride and *p*-toluene sulfonyl chloride show less reactivity than acetic anhydride and acyl chlorides [78].

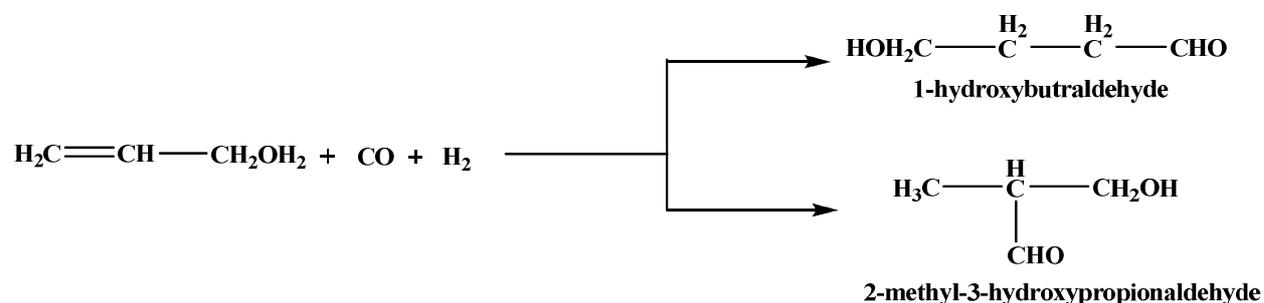


(37) **Bromination:** Reaction of methoxybenzene with N-bromosuccinimide in presence of Montmorillonite K 10 affords excellent yields of regiospecifically brominated product in solvent free condition [79] (Scheme-72).



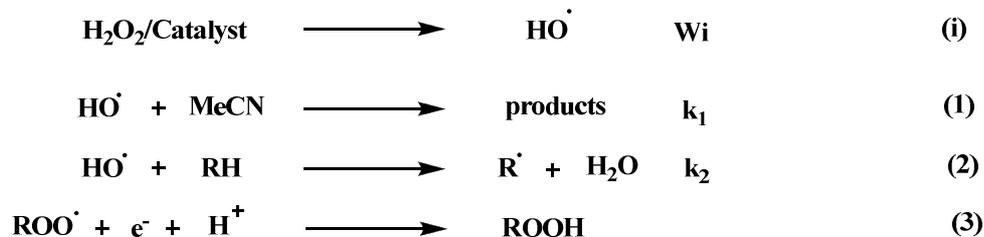
Scheme-72

(38) **Hydroformylation:** Hydroformylation of olefins to give corresponding non-branched aldehydes is an industrially important reaction. With heterogeneous catalyst system, rhodium catalyst anchoring to inorganic support such as montmorillonite clay, hydroformylation of allyl alcohol give hydroxybutyraldehyde (96%) and 2-methyl-3-hydroxypropionaldehyde (4%) at 70°C and 60 atm of equimolar mixture of CO + H₂ [80] (Scheme-73).



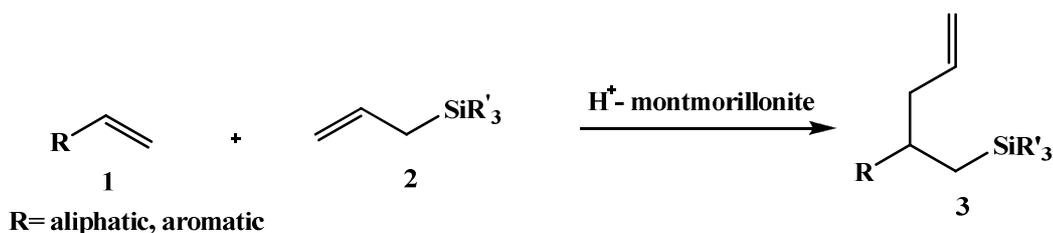
Scheme-73

(39) **Hydrogen Peroxide Oxygenation:** Hydroxylation and hydroperoxidation of saturated hydrocarbons is one of important goals of contemporary catalytic chemistry. Montmorillonites and aluminum oxide, Al₂O₃, catalyze alkane hydroperoxidation and olefin epoxidation with hydrogen peroxide. Alkanes afford alkyl hydroperoxides as main primary products which partially decompose to produce corresponding ketones and alcohols [81] (Scheme-74).

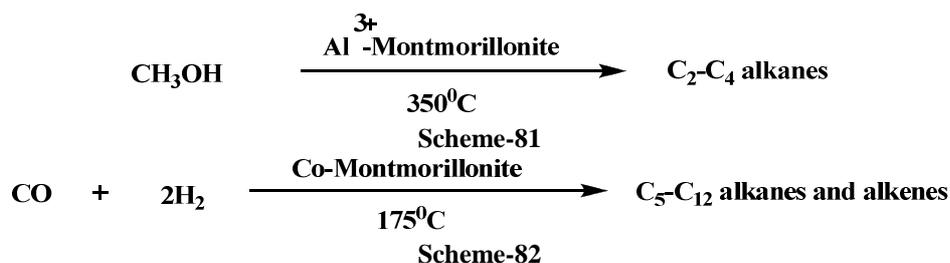


Scheme-74

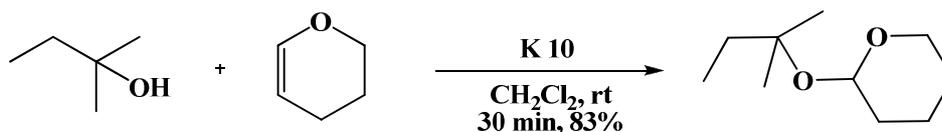
(40) **Allylsilylation:** Allylsilylation of an alkene is the only known procedure to install both silyl and allyl groups onto a carbon-carbon double bond directly. Proton-exchanged montmorillonite showed excellent catalytic performances for the allylsilylation of alkenes. For example, the reaction of *p*-chlorostyrene with allyltrimethylsilane proceeded smoothly to afford the corresponding allylsilylated product in 95% yield [82] (Scheme-75).



Scheme-75

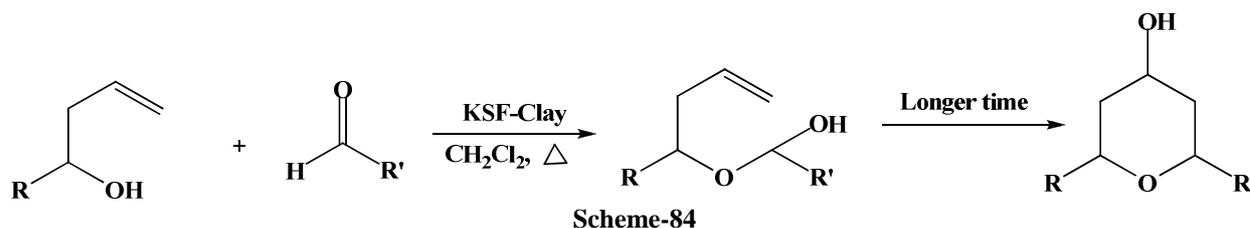
**(46) Miscellaneous reactions:**

(a) Protective tetrahydropyranylation of alcohols and phenols: With an excess of 3,4-dihydro-2H-pyran, in the presence of K 10 at room temperature, alcohols are transformed quantitatively into their tetrahydropyranyl derivatives (**Scheme-83**). Run in dichloromethane at room temperature, the reaction is complete within 5-30 min. The procedure is applicable to primary, secondary, tertiary and polyfunctional alcohols as well as to phenols [86].

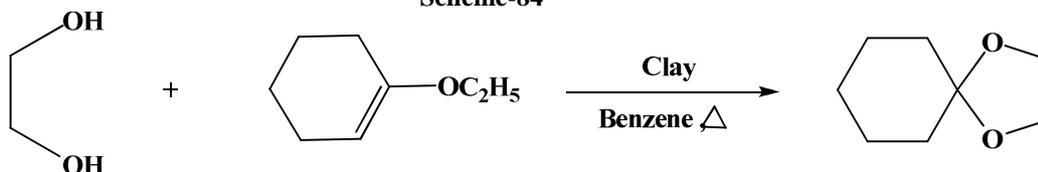


Scheme-83

(b) 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 [68] (**Scheme-85**).

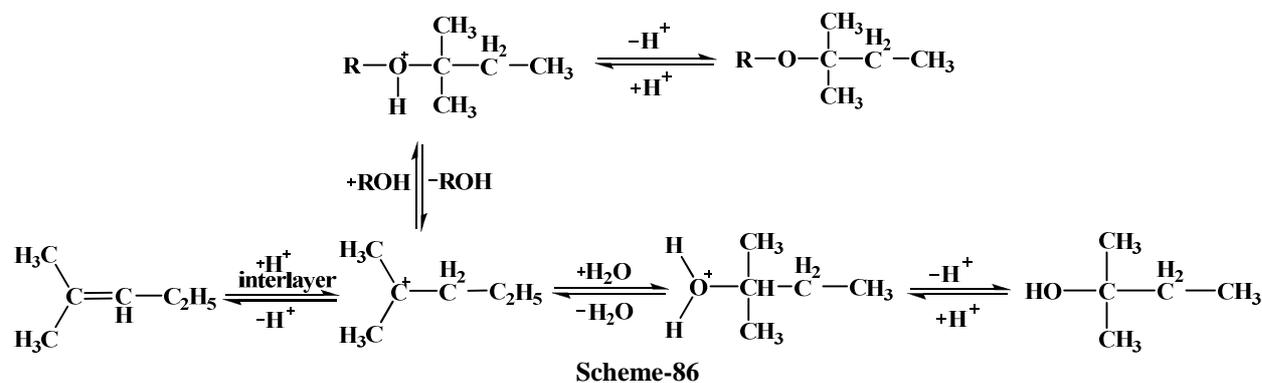


Scheme-84



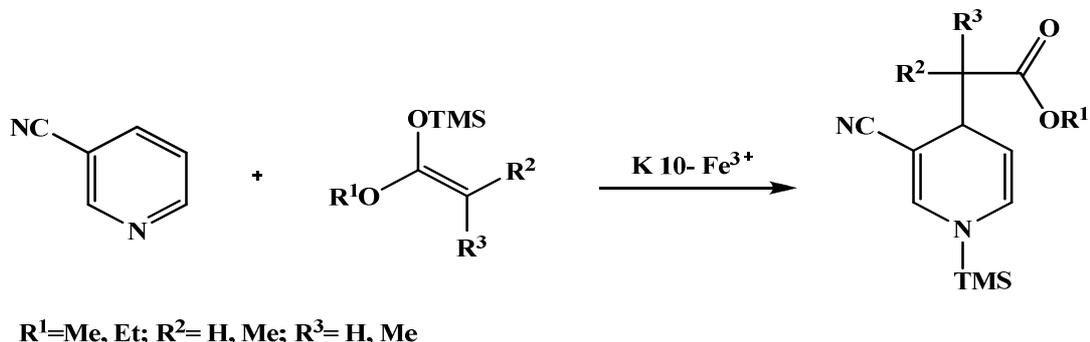
Scheme-85

(c) Reaction of 2-methylpent-2-ene with alcohols: Recently, Ballantine *et al.* (1981b) found that the reactions of alcohols with ion-exchanged montmorillonites give di-(alk-1-yl) ethers at 180°C through tertiary carbonium ion [87] (**Scheme-86**).



Scheme-86

(d) The coupling of silyl ketene acetals (enosilanes) with pyridine derivatives bearing an electron-withdrawing substituent, namely cyano, in the meta position is catalysed by iron montmorillonite and other similar solid-acid catalysis [88] (Scheme-87).



Scheme-87

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.

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