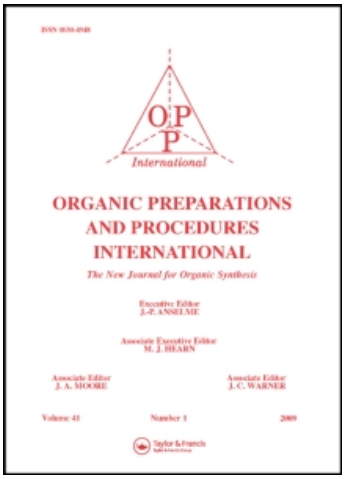

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APPLICATION OF CLAY CATALYSTS IN ORGANIC SYNTHESIS. A REVIEW

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APPLICATION OF CLAY CATALYSTS IN ORGANIC SYNTHESIS. A REVIEW

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INTRODUCTION

Environmental regulations and safety concerns have led to the development of environmentally benign methodologies.[1] Among the viable alternatives available for green synthetic methods, clays and clay-based catalysts in particular have attracted significant attention due to their extremely versatile properties. As aluminosilicates of layered structures, they provide several possibilities for synthetic applications and can be used as acid (cationic clays) or base (anionic clays) catalysts. In addition, the layered structure and ion-exchange capabilities allow the intercalation of different organic molecules, or the ion-exchange of specific metal ions, including metal complexes. The major goal of this review is to provide an overview on the application of clay-based catalysts in organic synthesis. The structural properties of clays and their synthesis or modifications will not be discussed. The use of clay-based materials in organic synthesis has a rather extensive history. The earlier period has been well reviewed in several comprehensive accounts.[1,2] Thus the present survey will concentrate on the new developments published in 1999-2007 period. The number of papers related to this topic, published in this period exceeds four hundred, attesting to the extraordinary interest in the use of these materials. Even though we are unable to cover all of these reports, our goal is to provide a comprehensive overview of synthetic applications of clay catalysts. Due to the nature of this work, emphasis will be placed on clay-based materials that are either commercially available or can be synthesized from such sources (mainly bifunctional clay catalysts). The two most common clay catalysts applied in organic synthesis are the K-10 and KSF-montmorillonites. Both are synthetic clays, produced from natural montmorillonites, and are available from most suppliers. The basic difference between these catalysts lies in their BET (Brunauer, Emmett and Teller adsorption isotherm used for quantitative determination of monolayer capacity from multilayer adsorption and also used for surface area determination) surface. K-10 has a substantially higher surface area (250

m^2g^{-1}) than KSF (10 m^2g^{-1}), while their acidity is comparable. The Hammett acidity constant of these materials is $H_0 \approx -8$, which corresponds approximately to the acidity of concentrated nitric acid. These two materials are used mostly to prepare other, usually bifunctional catalytic materials. Many of these derivatives are already commercially available under different trade names. The most common reagents and catalysts are *claycop*^{TM}, *clayzinc*^{TM}, *clayfen*^{TM}, *envirocat*^{TM}, etc. Some others can easily be prepared from these clays and common metal salts or metal complexes. Their preparation is usually simple and is provided in the original publications. Due to their physical nature, clays or clay-based catalysts absorb microwave energy and are excellent catalysts for microwave-assisted organic synthesis (MAOS).[3] As a consequence, many synthetic processes discussed in this work use microwave irradiation as energy input. The discussion of the effect of microwaves on clays and relevant materials, however, is beyond the scope of this review; the reader should consult leading references.[3]

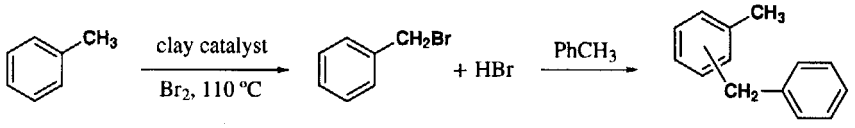
I. ACID CATALYSIS

1. Friedel-Crafts Reactions

The Friedel-Crafts reaction is one of the most important C-C bond forming reactions in organic chemistry, for both laboratory and industrial applications.[4] There are several effective and industrially applicable catalysts available. Although the application of traditional Lewis and Brønsted acid catalysts have resulted in an extensive number of excellent processes, these conventional catalysts do not usually conform to the current environmental standards. This has spurred extensive interest in the investigation of clays as catalysts for synthetic applications involving the Friedel-Crafts chemistry.

a) Alkylation

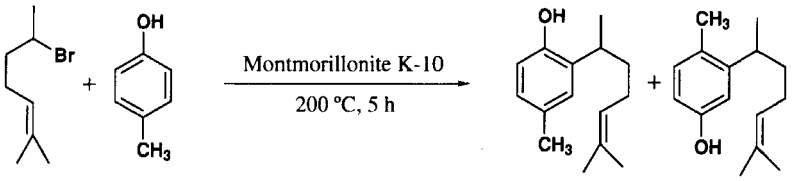
Industrially important benzyl toluenes have been synthesized by clay-catalyzed benzylation of toluene through bromination.[5] Using commercially available montmorillonite K-10 and bentonite catalysts, the products have been obtained in good yields in a continuous process. During the reaction the HBr formed is recycled and re-oxidized to bromine by air (*Scheme 1*).



Scheme 1

Yields up to 87%

Microwave-assisted alkylations of *p*-methylphenol and *m*-methylphenols with bromoheptenes using montmorillonite K-10 catalyst have been used in the synthesis of natural products, such as *elvirol* (*Scheme 2*), *curcuphenol*, *sesquichamaenol* in good yields.[6]

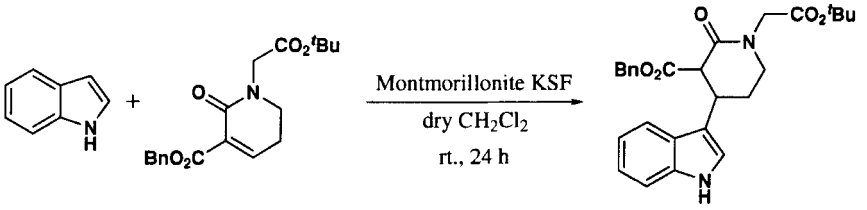


Elvirol 62%

25%

Scheme 2

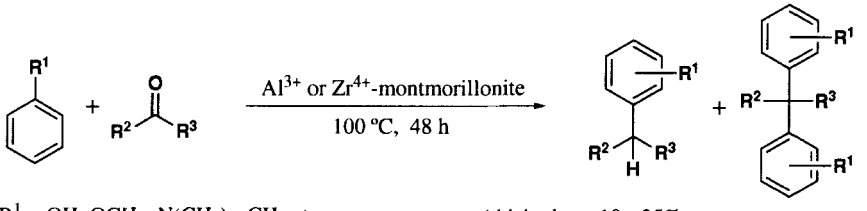
KSF, another frequently utilized montmorillonite, has been a very effective catalyst for the alkylation of indoles with α,β-unsaturated ketones and esters. The reaction served as an important step during the synthesis of constrained pseudopeptides (*Scheme 3*).[7]



Scheme 3

80% (*trans*/*cis* = 10:1)

Benzenoid aromatic compounds may also be alkylated with carbonyl compounds. Metal cation-exchanged montmorillonites effectively catalyzed the alkylation of activated aromatic compounds (phenol, anisole, veratrol, *p*-cresol) with aldehydes and ketones (*Scheme 4*).[8] The process has certain limitations; Al^{3+} and Zr^{4+}-montmorillonites exhibited significant activity, while Fe^{3+}, Zn^{2+}, H^+ and Na^+ ion-exchange did not result in effective catalysis.



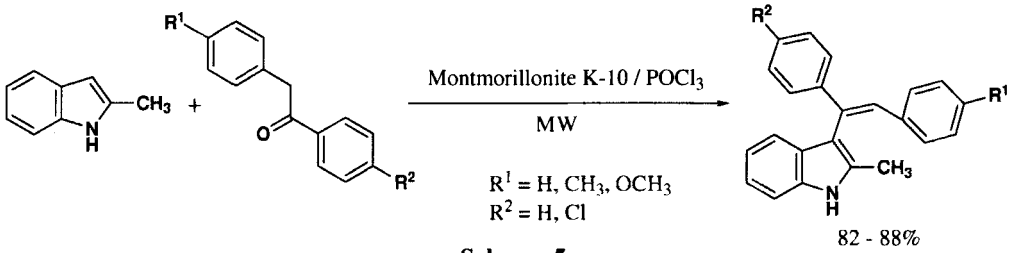
R^1 = OH, OCH_3, $N(CH_3)_2$, CH_3 etc.
R^2 = C_2H_5, C_3H_7, C_6H_5, C_4H_9, $CH_3(CH_2)_n$ etc.
R^3 = H, CH_3, C_2H_5

Aldehydes: 10 - 25%
Ketones : 30 - 78%

60 - 90%
12 - 25%

Scheme 4

The easy accessibility and biological activity of 3-substituted indoles makes them important target compounds. 3-Diarylvinylindoles were synthesized in good yields using phosphoryl chloride on montmorillonite K-10 under microwave conditions (*Scheme 5*).[9]

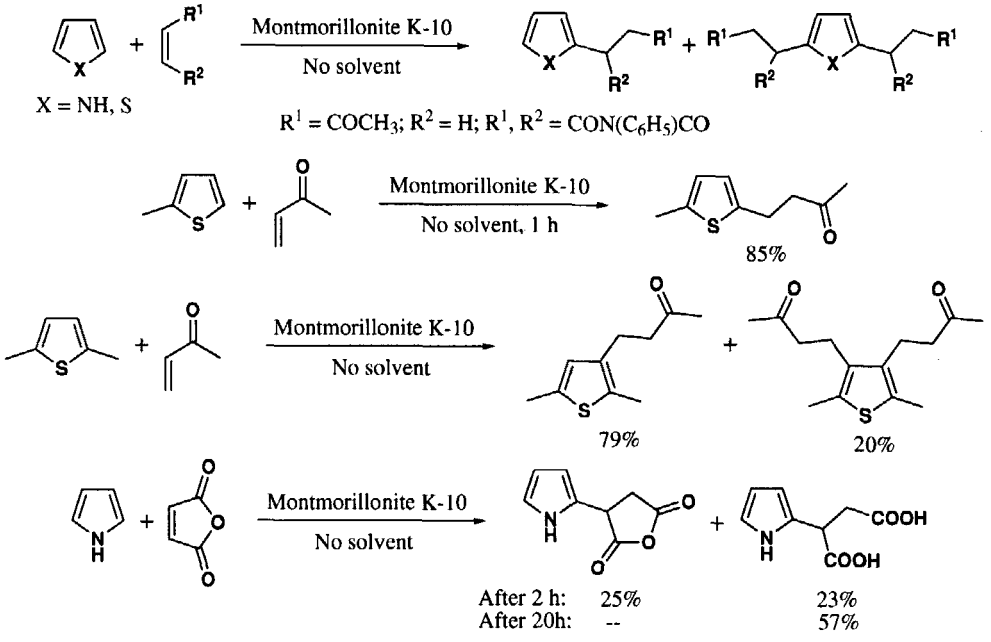


R^1 = H, CH_3, OCH_3
R^2 = H, Cl

82 - 88%

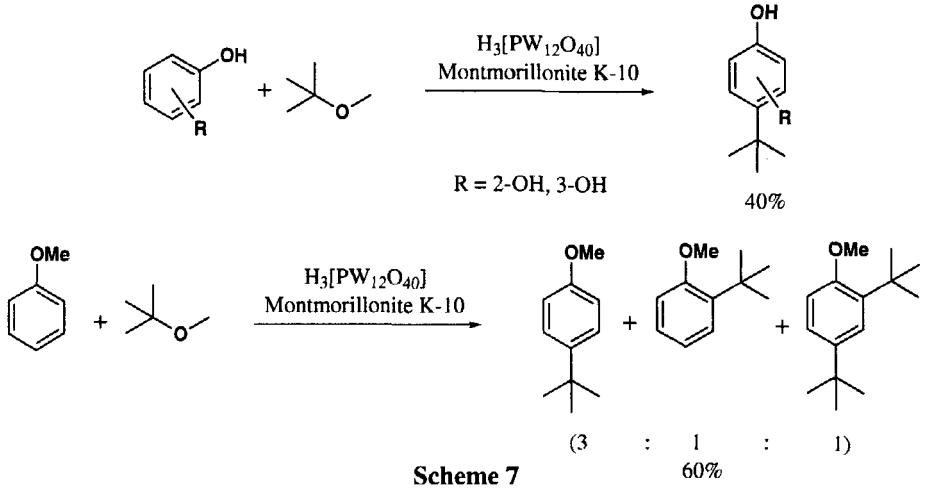
Scheme 5

The conjugate addition reactions of heteroaromatics to enones and alkynoates under solvent-free conditions, in the presence of montmorillonite K-10 lead to functionalization of pyrrole and thiophene nuclei, which are important compounds with wide applicability in the fields of bioactive compounds, organic semiconductors, addressable gene-chips, etc. This procedure may be used to prepare various *mono-* and *bis*-alkylated products (*Scheme 6*).[10]



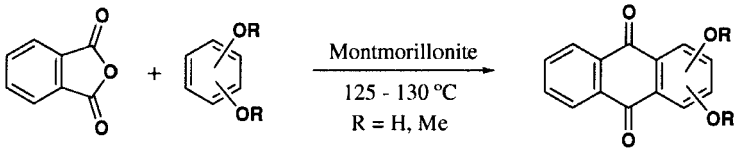
Scheme 6

Dodecatungstophosphoric acid, $H_3[PW_{12}O_{40}]$ (20% w/w), supported on montmorillonite K-10 clay was used to synthesize industrially important *tert*-butylated dihydroxy- and alkoxybenzenes from catechol, resorcinol, anisole and methyl *tert*-butyl ether (*Scheme 7*).[11]



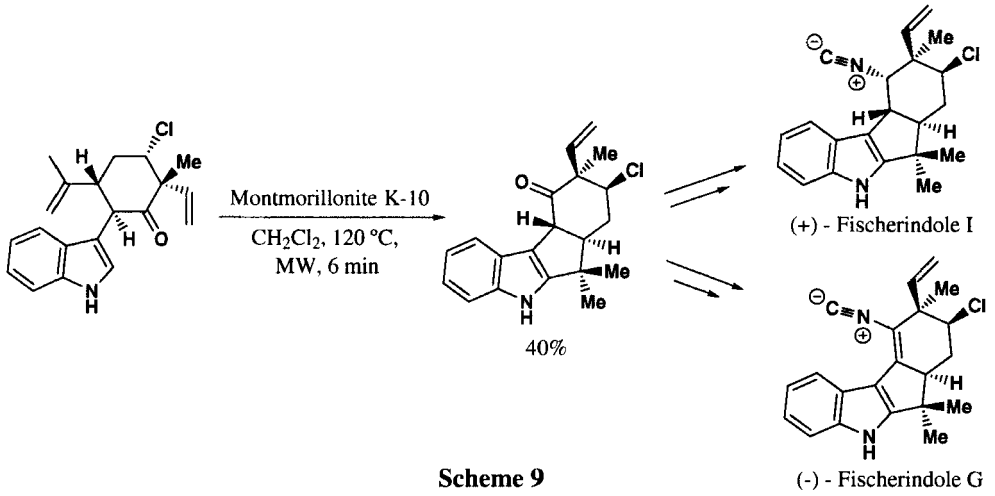
Scheme 7

Various anthraquinone derivatives were prepared from phthalic anhydride and substituted benzenes by using montmorillonite clays, though montmorillonite K-10 performed better than montmorillonite KSF (*Scheme 8*).[12]



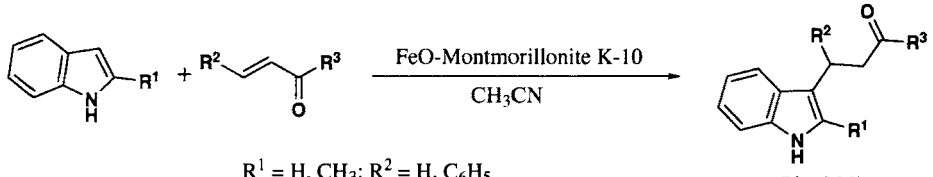
Scheme 8

A montmorillonite K-10 catalyzed process was used to carry out an electrophilic annelation on the indole moiety for the synthesis of indole alkaloids (+)-*fischerindole I* and (-)-*fischerindole G* (*Scheme 9*).[13] This process was later extended by the authors to the synthesis (+)-*welwitindolinone A*.[14]



Scheme 9

Various α,β-unsaturated carbonyl compounds readily underwent Michael addition with indoles to give the corresponding 3-alkylated or 3-acylated indoles in the presence of Fe (III)-exchanged montmorillonite K-10. The alkylation proceeded with high yields and high selectivities (*Scheme 10*).[15]

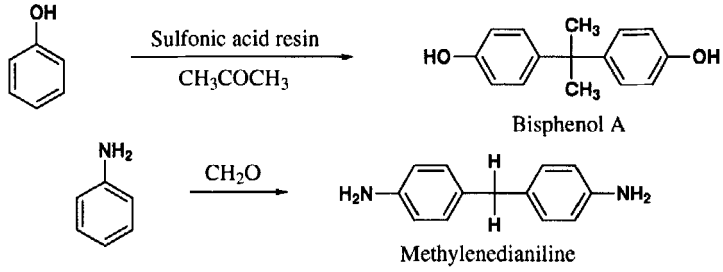


R^1 = H, CH_3; R^2 = H, C_6H_5
R^3 = CH_3, C_6H_5, 4-$CH_3OC_6H_5$, 3,4-$(OCH_2O)C_6H_3$
R^2- R^3 = $(CH_2)_3$

Scheme 10

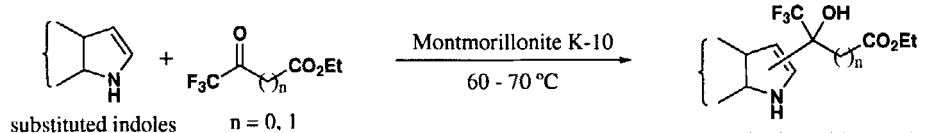
b) Hydroxyalkylation

An important synthetic step towards the preparation of many raw materials and fine chemicals is the hydroxyalkylation of aromatic compounds with ketones or aldehydes, containing different substituents to generate important compounds such as bisphenols and methylenedianiline. In industrial practice, bisphenol A is produced by solid sulfonic acid resin catalysts (*Scheme 11*).[16]



Scheme 11

Another recent example is the hydroxyalkylation of *N*-heteroaromatics such as pyrroles and indoles with ethyl trifluoropyruvate and ethyl trifluoroacetoacetate in toluene by montmorillonite K-10 catalysis in a closed pressure vessel under mild experimental conditions (*Scheme 12*).[17]



substituted indoles and pyrroles

n = 0, 1

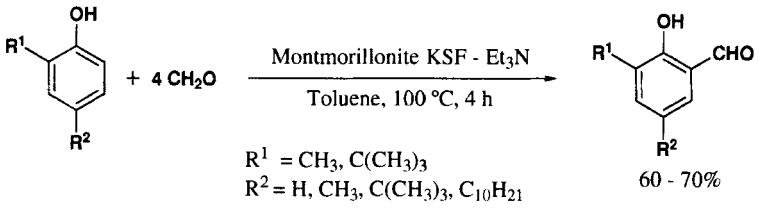
2-substitution with pyrroles
3-substitution with indoles
yields: 85 - 97%

Scheme 12

The reaction provided excellent yields and selectivities, and no by-product formation was observed. The reaction rates are extremely high (97% yield in 6 minutes) compared to other alternative methods.[18]

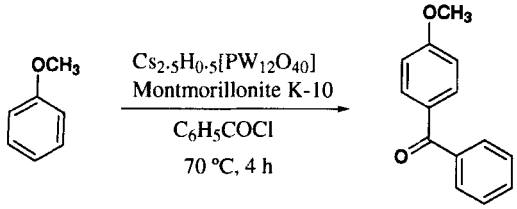
c) Acylation

Salicylic aldehydes are important intermediates for the synthesis of a large number of organic compounds such as coumarins, benzofurans, salen derivatives and many industrially useful metal extractants. As such, the development of contemporary and environmentally sustainable methods is highly desirable. In a recent example, montmorillonite KSF-triethylamine complex was used as a heterogeneous and reusable catalyst for the synthesis of salicylic aldehydes from phenols and formaldehyde (*Scheme 13*).[19]



Scheme 13

The cesium salt of dodecatungstophosphoric acid supported on montmorillonite K-10 acted as a catalyst for the acylation of anisole with benzoyl chloride. The main advantage of this catalyst is that it can be reused without any further chemical reactivation (*Scheme 14*).[20]

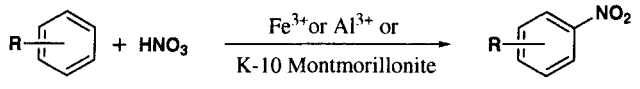


Scheme 14

2. Other Aromatic Electrophilic Substitutions

a) Nitration

Several organic intermediates required in large quantities in the fine chemical industry are produced by nitration of aromatic compounds. Selective nitration of aromatic compounds can be carried out with high yields using nitric acid and modified clays. Among these, a Fe^{3+}-ion exchanged montmorillonite catalyst was the most effective. In the case of substituted aromatics, the 4-substituted products formed in excess (*Scheme 15*).[21]

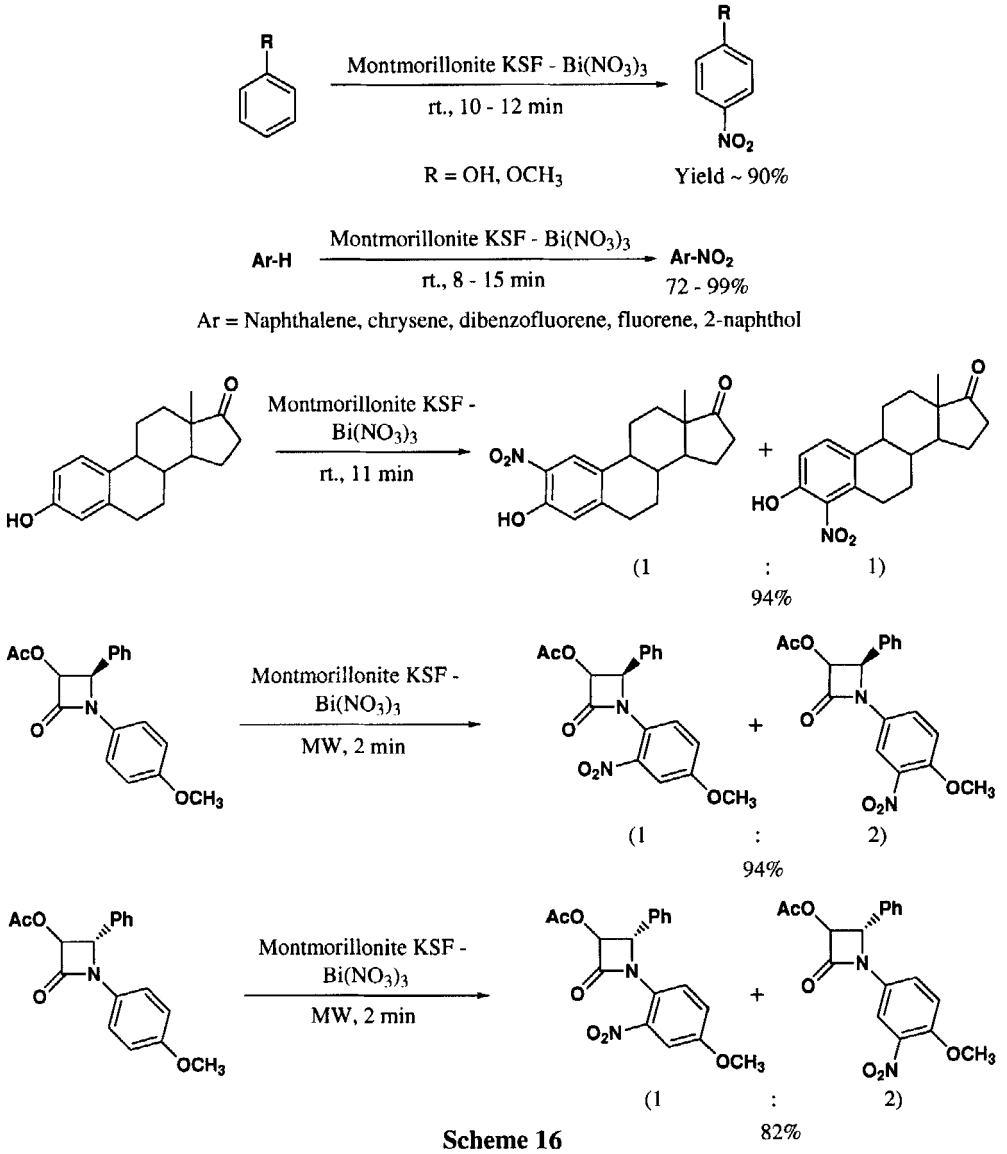


Yields up to 95%
4- > 2- >> 3-

R = H, CH_3, Cl, Br, I, C_3H_7, OCH_3

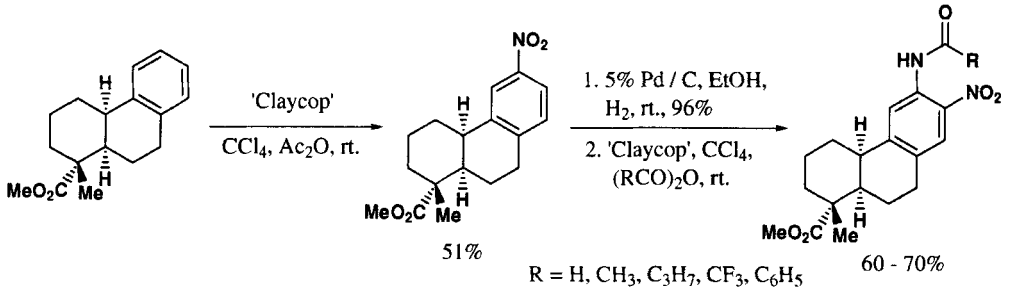
Scheme 15

Aromatic nitration was carried out in high yields using bismuth nitrate supported on montmorillonite KSF. The reaction was carried out by mixing the reactants and the catalyst together in a solvent and, after thorough mixing, the solvent was evaporated. On occasions when this reaction remained incomplete, the reaction mixture was subjected to microwave irradiation under solvent-free conditions. This method was used for the nitration of polycyclic aromatic hydrocarbons, steroids and β-lactams (*Scheme 16*).[22]



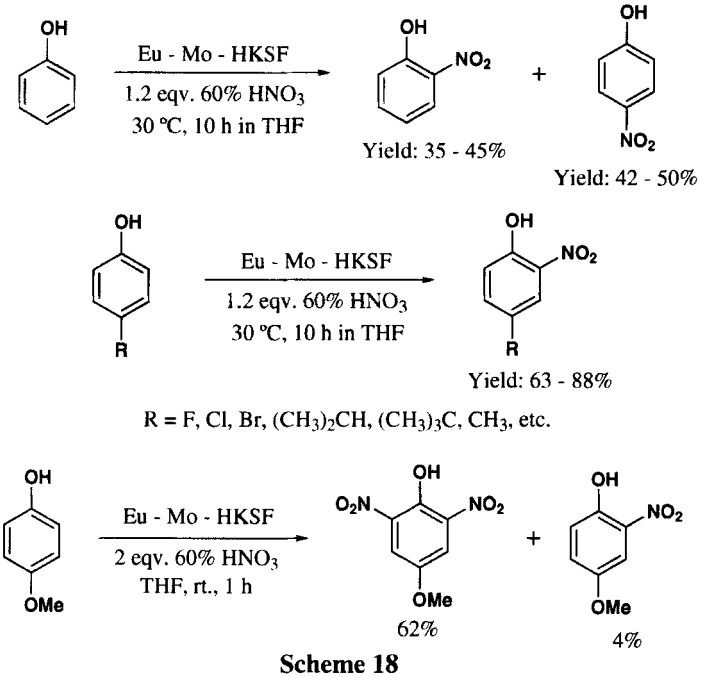
Scheme 16

Montmorillonite impregnated with copper nitrate, 'claycop', was used in the selective nitration of methyl *cis*-deisopropyldehydroabietate in its 12-position. The nitro-compound was then reduced to the corresponding amine and the amine was subjected to combined acetylation and nitration using 'claycop', and the appropriate carboxylic acid anhydride in carbon tetrachloride to give 12-acylamino-13-nitro compounds in 60-70% yields (*Scheme 17*).[23]



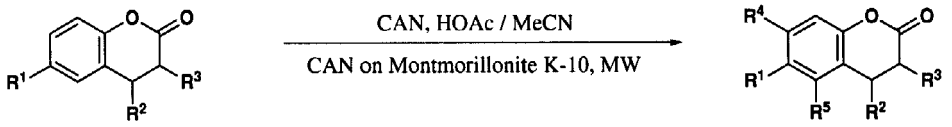
Scheme 17

Metal modified montmorillonite KSF, prepared from different metal salts (V, Mo, W, Sc, La, Yb, Eu, In, Bi, Ti, Zr, Hf) and KSF or nitric acid-treated HKSF acts as a catalyst for the nitration of phenolic compounds with 60% nitric acid. The catalyst could be recovered and used several times in the nitration (*Scheme 18*).[24]



Scheme 18

An effective and convenient nitration of coumarins, particularly of deactivated coumarin derivatives, was achieved in microwave-assisted ammonium cerium (IV) nitrate (CAN) deposited on montmorillonite K-10 catalyzed reactions (*Scheme 19*).[25]



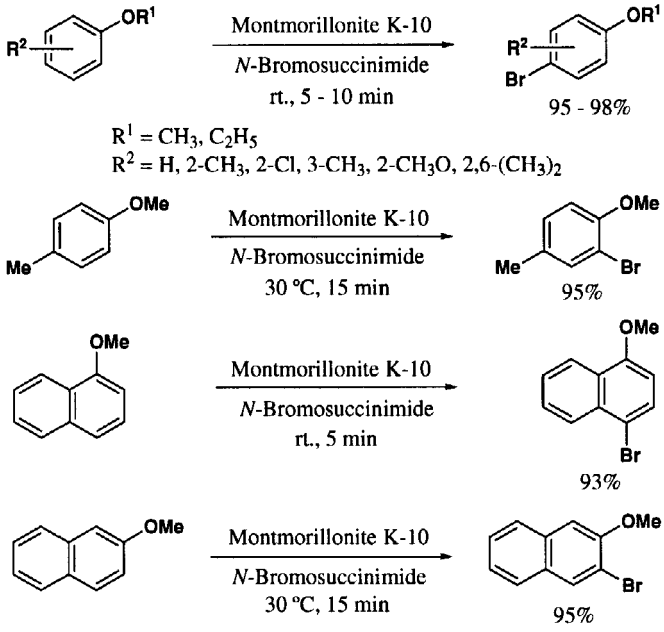
R^1 = H, OH, OCH_3
R^2 = H, CH_3, OH
R^3 = H, OH, OCH_3

R^1 = H, OH, OCH_3
R^2 = H, CH_3, OH
R^3 = H, OH, OCH_3
$R^4 = R^5$ = H, NO_2

Scheme 19

b) Halogenation

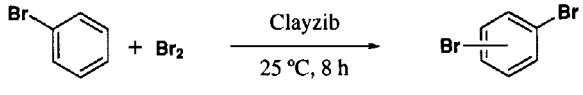
Bromination of methoxybenzenes and naphthalenes with *N*-bromosuccinimide was catalyzed by montmorillonite K-10 to give regiospecifically brominated products in excellent yields under mild and solvent-free conditions (*Scheme 20*).[26]



R^1 = CH_3, C_2H_5
R^2 = H, 2-CH_3, 2-Cl, 3-CH_3, 2-CH_3O, 2,6-$(CH_3)_2$

Scheme 20

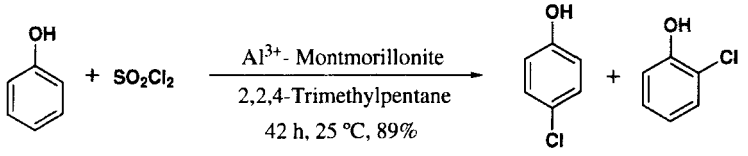
Bromination of aromatic substrates using zinc bromide-montmorillonite K-10 catalyst (*clayzib*) has been described as an environmentally friendly alternative for the synthesis of bromoaromatics (*Scheme 21*).[27] The catalytic system gave excellent yields under very mild reaction conditions. Though the bromination proceeded well with *clayzib*, mesoporous silica gel gave the best selectivities and good reaction rates with other substituted benzenes as well.



Yields up to 99%
4- / 2- ratio up to 11

Scheme 21

Al^{3+}-ion exchanged montmorillonite was used efficiently as a catalyst in the presence of SO_2Cl_2 in 2,2,4-trimethylpentane for the selective 4-chlorination of phenols at room temperature (*Scheme 22*).[28] When this methodology was extended to *ortho*-cresol and anisole, it gave ~ 98% and ~ 94% conversions. The ratio of the 4/2 substitutions was 6.1/1 and 7.9/1 respectively.

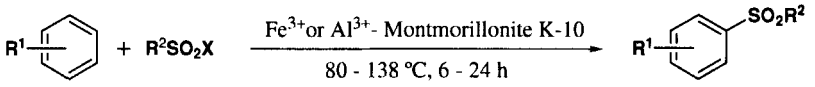


(5.7 : 1)

Scheme 22

c) Sulfonylation

Sulfonylation of aromatic compounds to sulfones was carried out using various metal ion-exchanged K-10 montmorillonites. The modified clay served as a mild and efficient catalyst for these transformations (*Scheme 23*).[29]



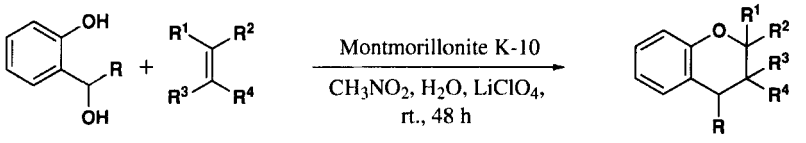
60 - 94%

$R^1 = CH_3, C_6H_5, CH_3, 1,3,5\text{-}(CH_3)_3$
$R^2 = CH_3, C_6H_5, 4\text{-}CH_3C_6H_4$
X = Cl, OH, OSO_2R

Scheme 23

3. Cycloaddition Reactions

Diels - Alder reaction is an important reaction in organic chemistry and wet montmorillonite K-10 has been used as a catalyst for the intermolecular hetero Diels-Alder reaction between unactivated alkenes and *in situ* genetrated 2-quinomethanes to give various chromane skeletons in $LiClO_4$-CH_3NO_2 solution (*Scheme 24*).[30]



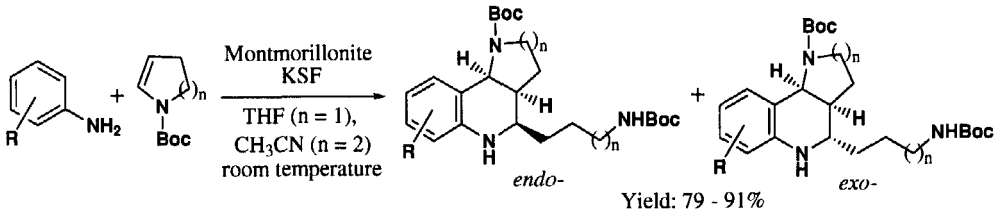
R = H, CH_3

$R^1 = R^2 = R^3 = R^4 = C_6H_5CH{=}CH$, Cyclohexyl, $4\text{-}CH_3C_6H_4CH{=}CH$, 2,3-Dimethylbut-2-enyl, etc.

78 - 99%

Scheme 24

The synthesis of various quinoline or naphthyridine derivatives from arylamines and ene-carbamates was carried out with montmorillonite KSF as a catalyst (*Scheme 25*).[31] The products were obtained in excellent yields and moderate diastereoselectivity.

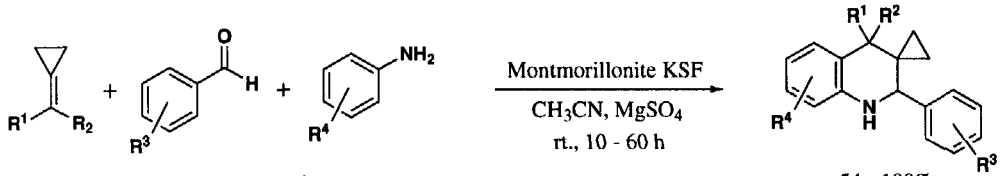


Yield: 79 - 91%

R = H, 4-CH_3, 4-Cl, 3,4-$(CH_3O)_2$, 4-F, 4-CO_2CH_3, etc

Scheme 25

A simple and efficient synthesis of spirocylopropyl ring containing quinoline derivatives were achieved by a three component *aza*-Diels-Alder reactions of arenecarbaldehydes, arylamines and methylenecyclopropanes in the presence of montmorillonite KSF under mild reaction conditions. Various substituted quinolines have been synthesized using this method (*Scheme 26*).[32]

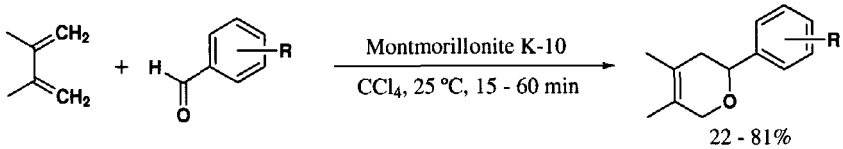


54 - 100%

R^1 = 4-$CH_3C_6H_4$, 4-$CH_3OC_6H_4$, 4-$C_2H_5OC_6H_4$
R^2 = CH_3, C_6H_5, 4-$CH_3C_6H_4$, 4-$CH_3OC_6H_4$
R^3 = H, 4-CH_3O, 4-Cl, 4-NO_2
R^4 = H, 3-CF_3, 2-CH_3O, 4-C_2H_5O

Scheme 26

A hetero Diels–Alder reaction of 2,3-dimethyl-1,3-butadiene with substituted benzaldehyde derivatives was achieved in the presence of montmorillonte K-10 at room temperature (*Scheme 27*).[33]



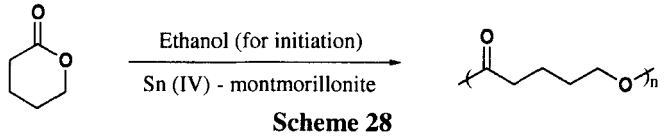
22 - 81%

R = H, 2-CH_3O, 2-C_2H_5O, 2-F, 2-Cl, 2-Br, 2-CN, 2-NO_2, 4-Cl, 4-NO_2

Scheme 27

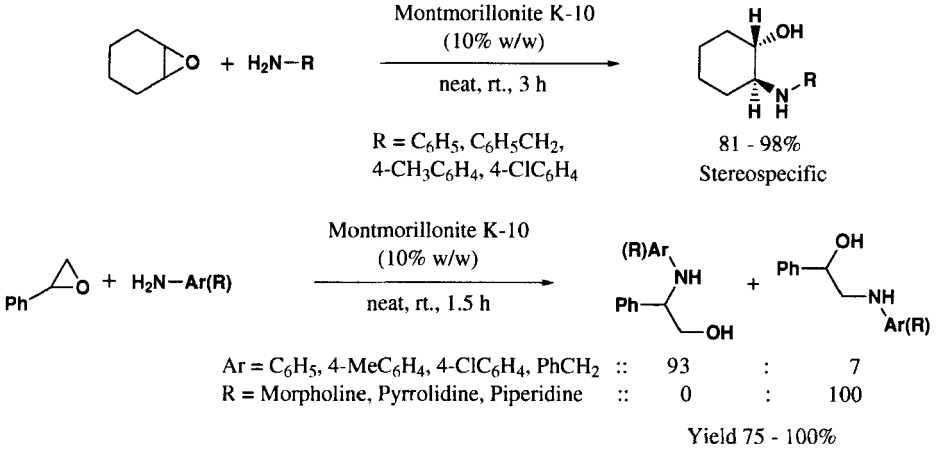
4. Ring-Opening - Ring Closure

The ring–opening polymerization of δ-valerolactone to polymeric products with controlled molecular weights was catalyzed by tin (IV) ion-exchanged montmorillonite in a solvent free system, although a minute amount of ethanol was used to initiate the reaction. The aluminium (III)- and iron (III)-exchanged montmorillonites were also effective for the polymerization of δ-valerolactone (*Scheme 28*).[34]



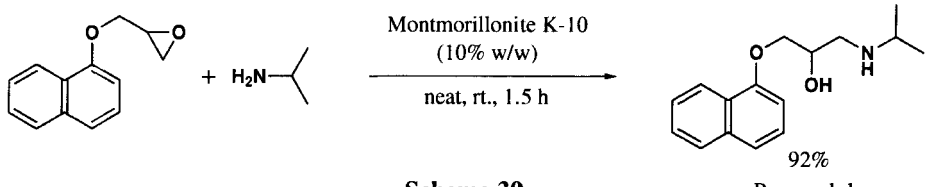
Scheme 28

The ring opening of epoxides by amines were carried out efficiently in the presence of montmorillonite K-10 providing amino alcohols with excellent regio- and stereoselectivity. The regioselectivity for unsymmetrical epoxides was controlled by electronic and steric factors associated with the epoxides and the amines. It provides an improved and efficient method for the preparation of β-aminoalcohols (*Scheme 29*).[35]



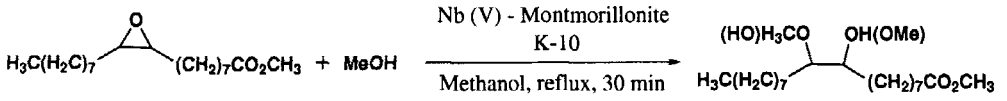
Scheme 29

The above general methodology was utilized for the preparation of propanolol, a β-adrenoreceptor antagonist (*Scheme 30*).[35]



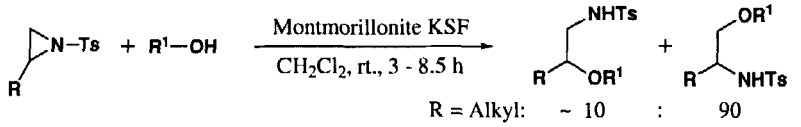
Scheme 30

Niobium(V) ion-exchanged montmorillonite K-10 was used to obtain β-hydroxyethers by the alcoholysis with methanol of epoxidized methyl oleate under reflux conditions (*Scheme 31*). The reaction resulted in practically quantitative product formation, however, the regioseletivity of the transformation was not discussed.[36]

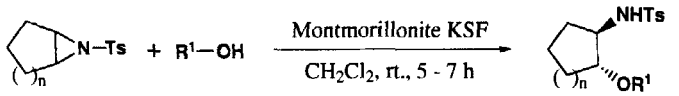


Scheme 31

Montmorillonite KSF was applied for regioselective ring opening of arylaziridines using alcohols. At ambient temperature, nucleophilic attack on the benzylic position of aryl-*N*-tosylaziridines was favored and the reaction gave the corresponding β-aminoethers in high yields. In contrast, alkyl-*N*-tosylaziridines, predominantly underwent terminal attack. Cycloalkyl-*N*-tosylaziridines also afforded the corresponding β-aminoethers (*Scheme 32*).[37]



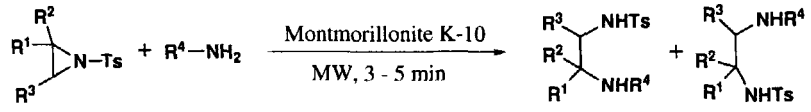
R = C_6H_5, 4-$CH_3C_6H_4$, 2-naphthyl,4-ClC_6H_4, cyclohexyl, C_4H_9
R^1 = CH_2=$CHCH_2$, CH_3CH=$CHCH_2$, C_2H_5, C_6H_5CH=CH, $C_6H_5CH_2$, etc.



R^1 = CH_2=$CHCH_2$, CH_3CH=$CHCH_2$, etc.

Scheme 32

Regio- and stereoselective ring-opening of *N*-tosylaziridines with amines provided the corresponding achiral and chiral diamines in high yields. The reaction was carried out with montmorillonite K-10 catalysis and under solvent-free microwave conditions (*Scheme 33*).[38]



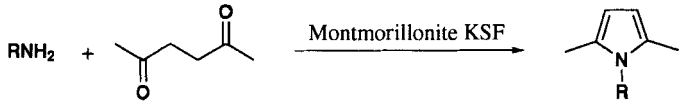
R^1 = C_6H_5, CH_3; R^2 = H, $COOCH_3$; R^3 = H, C_6H_5; R^1, R^3 = Cyclohexyl;
R^4 = C_6H_5, 4-$CH_3C_6H_4$, 4-$CH_3OC_6H_4$, $C_6H_5CH_2$, C_4H_9

Scheme 33

Chiral alkylphenethylammonium ion-exchanged K-10[39] and Wyoming montmorillonites[40] were used to initiate enantioselective ring-opening of epoxides. The reactions provided high yields under mild conditions with moderate enantioselectivities.

Simple syntheses of substituted alkyl- and arylsulfonylpyrroles can be carried out with K-10 and KSF catalysis. A modified Paal-Knorr method induced by montmorillonite KSF clay was used for the synthesis of substituted pyrrole derivatives from 2,5-hexanedione

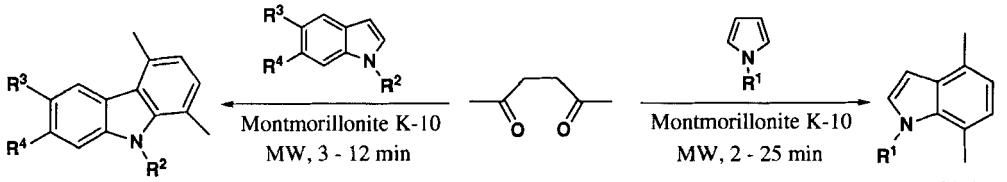
and various amines (*Scheme 34*).[41] This method was later extended for the synthesis of other pyrrole derivatives.[42]



R = C_6H_5, 4-$CH_3OC_6H_4$, 6-chrysenyl, 1-naphthyl, 1-anthracenyl, 1-prenyl, 9-phenanthrenyl, 2-pyridyl, $C_6H_5CH_2$

Scheme 34

This technology can also be applied to electrophilic annelation of indoles and pyrroles with 2,5-hexanedione by microwave-assisted K-10 catalysis (*Scheme 35*).[43] Compared to the examples described above, these reactions occurred in very short times due to

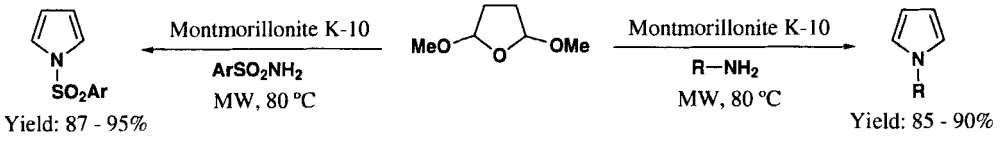


R^1 = H, CH_3, C_4H_9, C_6H_5, $C_6H_5CH_2$, C_6H_{11}, $C_6H_5(CH_3)CH$
R^2 = H, CH_3
R^3 = H, CH_3, I, Cl, Br, CH_3O
R^4 = H, CH_3

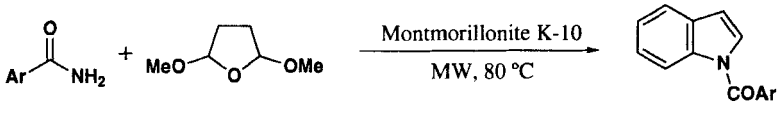
Scheme 35

the use of microwave activation. The approach is a highly effective new synthetic method for the preparation of indoles and carbazoles. The clay-catalyzed approach appears to be an efficient environmentally benign alternative to traditional methods such as a recent triflic-acid catalyzed method.[44]

This method has recently been extended for the selective one-pot synthesis of unsubstituted *N*-sulfonylpyrroles and *N*-acylindoles, using 2,5-dimethoxytetrahydrofuran as the alkylating agent (*Scheme 36*).[45,46]



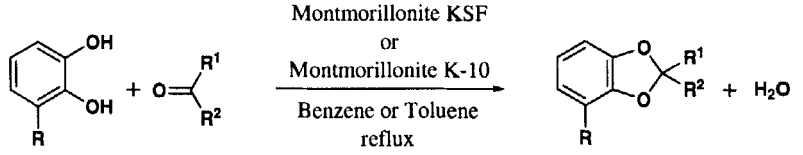
R = C_6H_5, thiazol-2-yl, 1-biphenyl-2-yl, cyclohexyl, 2-chloropyridin-3-yl, hept-2-yl, 1-phenylethyl, 3-$CF_3C_6H_4$, $C_6H_5CH_2$, indol-3-yl-$(CH_2)_2$, $(CH_3)_3C$
Ar = C_6H_5, 4-$CH_3C_6H_4$, 2-$CH_3C_6H_4$, 4-$NO_2C_6H_4$, 4-$CH_3OC_6H_4$, 4-ClC_6H_4, CH_3



Ar = C_6H_5, 4-$CH_3C_6H_4$, 4-$CH_3OC_6H_4$, 4-$NO_2C_6H_4$, 4-FC_6H_4, 4-ClC_6H_4, 4-$CF_3C_6H_4$, 4-$PC_6H_5C_6H_4$, naphth-2-yl

Scheme 36

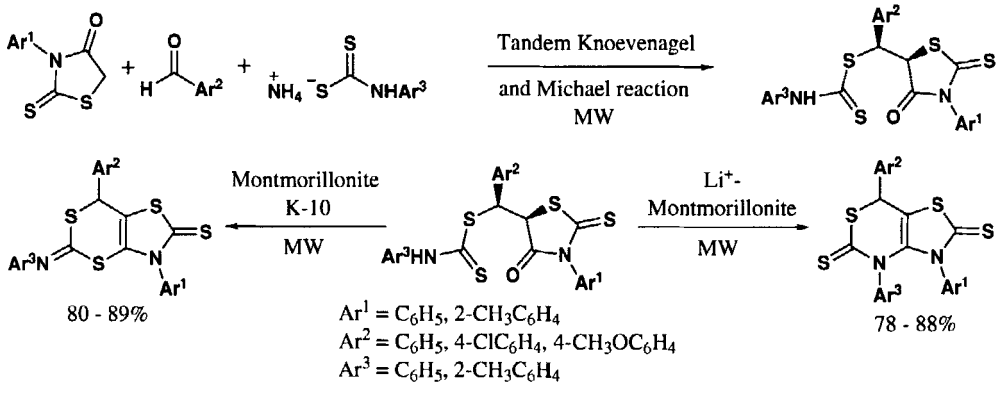
Bifunctional aromatic and aliphatic compounds also readily undergo cyclizations in the presence of clay catalysts. Montmorillonite KSF or K-10 catalysts were used for the reaction of catechols and pyrogallols with aldehydes and ketones to synthesize a series of 2-substituted and 2,2-disubstituted 1,3-benzodioxoles in moderate to good yields (*Scheme 37*).[47]



R = H, OH
R^1 = H, CH_3, C_2H_5, C_4H_9, $CH(CH_3)C_2H_5$, $CH(CH_3)_2$, C_5H_{11}, C_6H_{13}, $CH_2CO_2C_2H_5$, C_6H_5, etc.
R^2 = H, CH_3, $CH(CH_3)_2$, C_6H_5, 4-$CH_3OC_6H_4$, etc.

Scheme 37

In a recent approach, an intermediate compound obtained by a tandem Knoevenagel and Michael reaction of 3-arylrhodanines, aromatic aldehydes and ammonium *N*-aryldithiocarbamates was subjected to chemoselective intramolecular heterocyclization in the presence of montmorillonite K-10 and Li^+-montmorillonite to give thiazolo-1,3-dithiines and thiazolo-1,3-thiazines (*Scheme 38*)[48] in good to excellent yields.

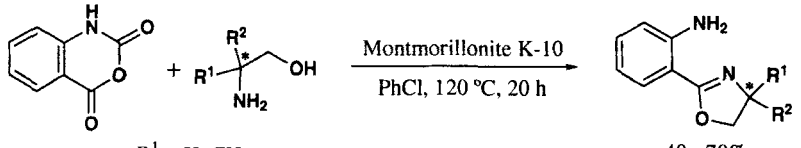


Ar^1 = C_6H_5, 2-$CH_3C_6H_4$
Ar^2 = C_6H_5, 4-ClC_6H_4, 4-$CH_3OC_6H_4$
Ar^3 = C_6H_5, 2-$CH_3C_6H_4$

Scheme 38

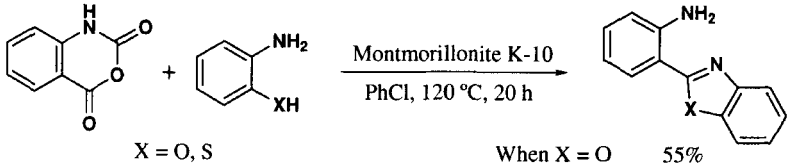
The combination of a ring opening–cyclization domino reaction catalyzed by montmorillonite K-10 is an efficient method for the preparation of 2-(2'-aminophenyl) oxazolines and a series of chiral derivatives from isatoic anhydride. Unlike many other acid-catalyzed reactions, the reaction with montmorillonite K-10 catalysis proceeded with retention of configuration of the chiral centers. The polymer-supported isatoic anhydride afforded the corresponding analogues (*Scheme 39*).[49]

The synthesis of several types of condensed benzo[*N,N*]-heterocycles such as benzimidazoles, benzodiazepines, quinoxalinones by a microwave-assisted solvent-free montmorillonite K-10 catalyzed method was also achieved. The approach is based on the reactions of a wide



R^1 = H, CH_3
R^2 = H, CH_3, $CH(CH_3)_2$, C_6H_5, $CH(CH_3)C_2H_5$, $CH_2C_6H_5$

40 - 70%

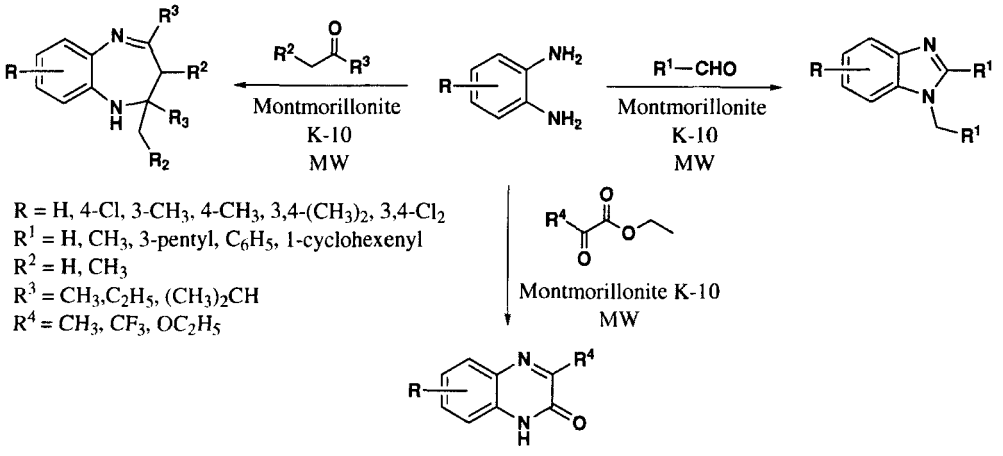


X = O, S

When X = O 55%
When X = S 58%

Scheme 39

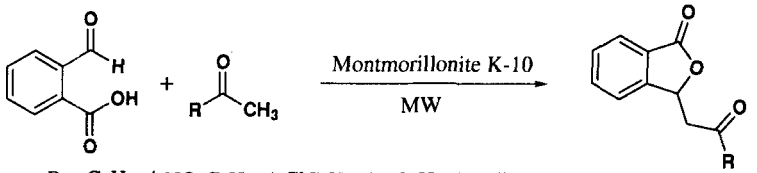
variety of 1,2-phenylenediamines with ketones, aldehydes and bifunctional reagents such as α-ketoesters, respectively. The products were obtained in very high yields (up to 98%) and with excellent selectivities in very short times (*Scheme 40*).[50]



R = H, 4-Cl, 3-CH_3, 4-CH_3, 3,4-$(CH_3)_2$, 3,4-Cl_2
R^1 = H, CH_3, 3-pentyl, C_6H_5, 1-cyclohexenyl
R^2 = H, CH_3
R^3 = CH_3,C_2H_5, $(CH_3)_2CH$
R^4 = CH_3, CF_3, OC_2H_5

Scheme 40

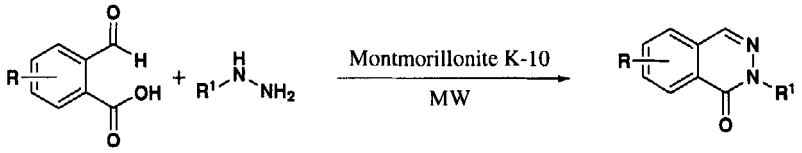
The synthesis of 3-phenacylphthalide derivatives has been accomplished by a solvent-free montmorillonite K-10 catalyzed process. The cyclization reactions were initiated by microwave irradiation and afforded the products in high yields (up to 98%) in short times (20-30 min) (*Scheme 41*).[51]



R = C_6H_5, 4-$NO_2C_6H_4$, 4-ClC_6H_4, 4-FC_6H_4, 2,4-di$CH_3C_6H_3$, 4-NCC_6H_4, 4-$CH_3OC_6H_4$,
and $(CH_3CH_2)C{=}O$, dimedone

Scheme 41

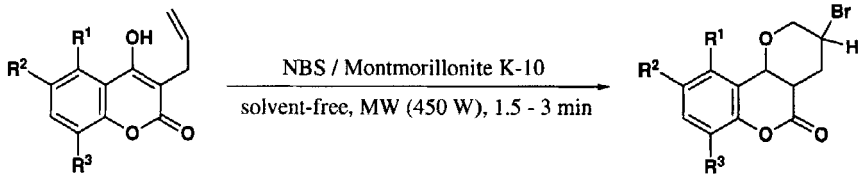
The synthesis of phthalazinones was achieved in microwave-assisted montmorillonite K-10 catalyzed solvent-free reactions. The approach is based on the reaction of 2-formylbenzoic acids with alkyl- and arylhydrazines (*Scheme 42*). The reactions provided the final products in very high yields (up to 98%) and with excellent selectivity, in short times (5-10 min).[52]



R = H, 2,3-di-CH_3O,
R^1 = H, C_6H_5, 3-$CH_3C_6H_4$, CH_3, 2-$CH_3OC_6H_4$, 2,5-di$(CH_3)C_6H_3$
2-$CH_3CH_2C_6H_4$, $(CH_3)_3C$, 4-$CH_3OC_6H_4$

Scheme 42

N-Bromosuccinimide on montmorillonite K-10 was used for the regioselective cyclization of 3-allyl-4-hydroxycoumarins under solvent-free conditions using microwave irradiation (*Scheme 43*).[53]



$R^1 = R^2 = R^3 = H$
$R^1 = R^2 = H$, $R^3 = CH_3$
$R^1 = R^3 = H$, $R^2 = CH_3$
$R^1 = R^3 = CH_3$, $R^2 = H$

80 - 96 %

Scheme 43

This method was extended for cyclization leading to the formation of different heterocyclic compounds (*Scheme 44*).[53]

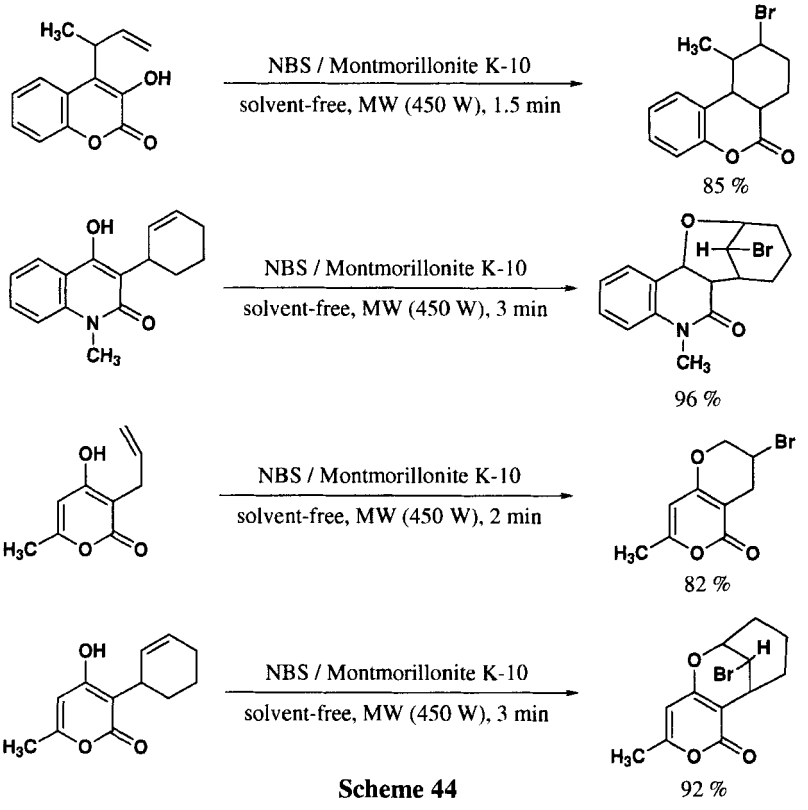
In a very recent paper Rousseau *et al.* described a multicomponent cyclization of aldehydes, 2-aminopyridine, and isocyanides catalyzed by montmorillonites K-10 and KSF. The reactions were initiated by microwave irradiation and conventional heating, respectively, and both yielded imidazo[1,2-a]pyridines in moderate to good yields (*Scheme 45*).[54]

5. Condensation

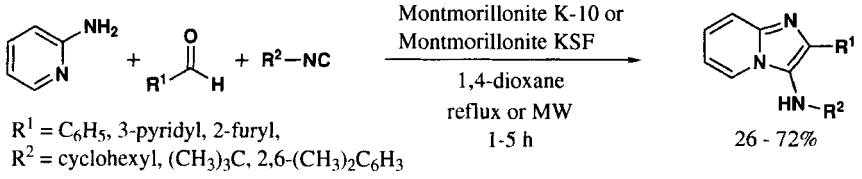
The Mukaiyama-aldol condensation of silyl enol ethers and ketene silyl acetals with various aldehydes was carried out in the presence of montmorillonite K-10 under solvent-free conditions or in water with moderate to good yields. Lower yields obtained with heteroaromatic aldehydes were attributed to the Brønsted acidic character of montmorillonite K-10 (*Scheme 46*).[55]

Coumarin-3-carboxylic acids were synthesized in high yield and with high selectivity from salicylic aldehyde and malonic acid in the presence of montmorillonite KSF. The dual acid-

base property of the clay catalyst played a crucial role in this reaction (*Scheme 47*).[56]

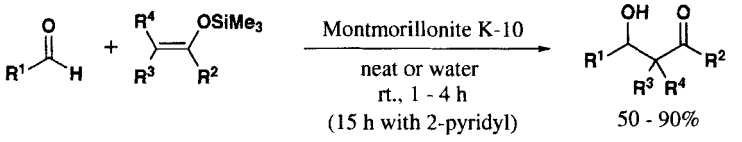


Scheme 44



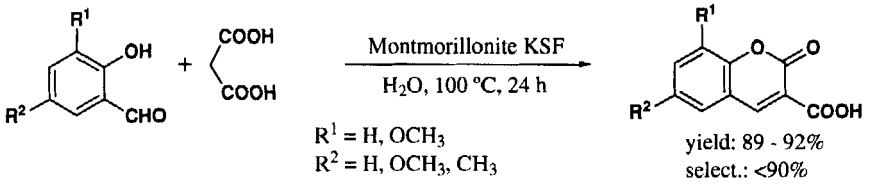
R^1 = C_6H_5, 3-pyridyl, 2-furyl,
R^2 = cyclohexyl, $(CH_3)_3C$, 2,6-$(CH_3)_2C_6H_3$

Scheme 45



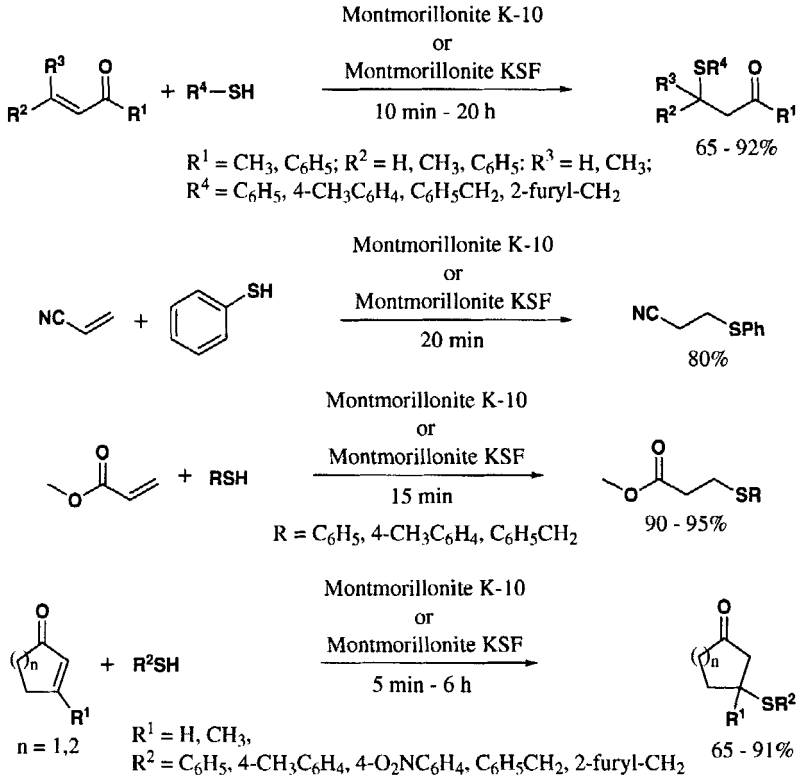
R^1 = C_6H_5, C_5H_{11}, $(CH_3)_2CH$, COOH, 2-pyridyl
R^2 = C_6H_5, 2-furyl, CH_3O
R^3 = H, CH_3
R^4 = H, CH_3
R^2, R^3 = Cyclopentyl, cyclohexenyl

Scheme 46



Scheme 47

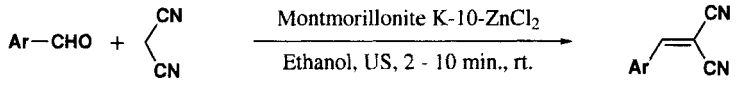
The conjugate addition of arylthiols or aralkylthiols with cyclic or acyclic α,β-unsaturated ketones, esters or nitriles occurred smoothly and efficiently in the presence of montmorillonite K-10 or montmorillonite KSF to form a carbon-sulfur bond (*Scheme 48*).[57]



Scheme 48

The Knoevenagel condensation of malononitrile with aromatic aldehydes was catalyzed by montmorillonite K-10-$ZnCl_2$ in anhydrous ethanol. The mixture was activated by ultrasonic irradiation (US), to give arylmethylenemalononitriles in good yields. The catalyst could be recycled twice without any significant decrease in activity (*Scheme 49*).[58]

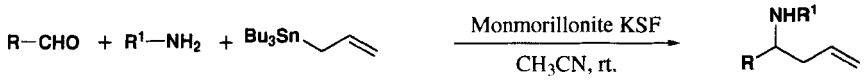
KSF montmorillonite acts as a heterogeneous solid acid catalyst under mild conditions for the synthesis of homoallylic amines, in excellent yields, by a three-component coupling reaction of aldehydes, amines and allyltributylstannane (*Scheme 50*).[59]



84 - 98%

Ar = C_6H_5, 4-HOC_6H_4, 2-ClC_6H_4, 3-ClC_6H_4, 4-ClC_6H_4, 2,4-$Cl_2C_6H_3$, 3-$O_2NC_6H_4$, 4-$O_2NC_6H_4$, 4-$CH_3OC_6H_4$, 3,4-$(OCH_2O)C_6H_3$, 4-HO-3-$CH_3OC_6H_3$, 4-$(CH_3)_2NC_6H_4$

Scheme 49

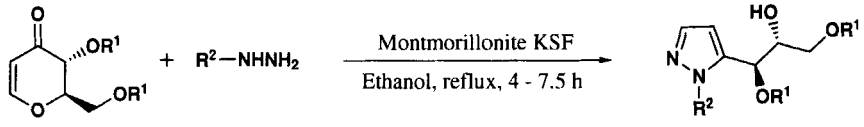


73 - 90%

R = C_6H_5, 4-$CH_3C_6H_4$, 2-naphthyl, 4-$CH_3OC_6H_4$, 4-$NO_2C_6H_4$, 4-ClC_6H_4, etc.
R^1 = C_6H_5, 4-ClC_6H_4, 4-FC_6H_4, 4-BrC_6H_4, etc.

Scheme 50

The condensation of arylhydrazines with 2,3-dihydro-4*H* pyran-4-ones, derived from (*D*)-glucal, yielded various chiral 5-substituted pyrazoles. These compounds form the core structure of many biologically active compounds. The reaction was carried out in the presence of montmorillonite KSF under mild experimental conditions in good yield and high selectivity (*Scheme 51*).[60]



57 - 86%

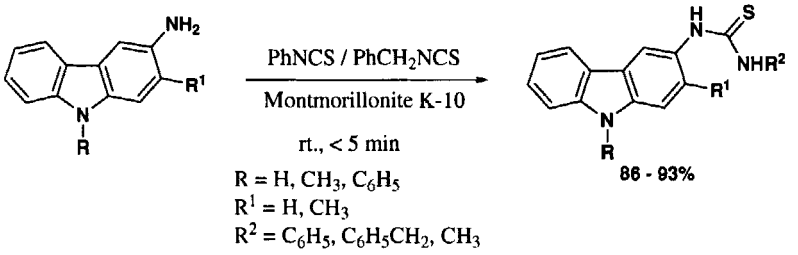
R^1 = CH_3CO, $C_6H_5CH_2$
R^2 = H, C_6H_5, 2,5-$Cl_2C_6H_4$, 2-$C_2H_5C_6H_4$, 4-ClC_6H_4, 3-ClC_6H_4, 4-$CH_3C_6H_4$

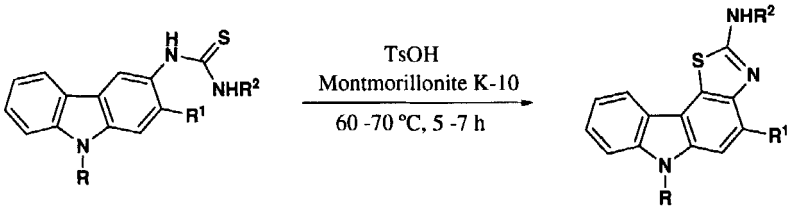
Scheme 51

3-Aminocarbazoles readily underwent a condensation with phenyl or benzyl isothiocyanates in the presence of montmorillonite K-10 at room temperature to give *N*-phenyl or *N*-benzyl thioureidocarbazoles. The thioureidocarbazoles were further transformed to 2-anilino or 2-benzylaminothiazolo[4,5-*c*]carbazoles, by heating them at 60-70 °C, in the presence of 4-toluene sulfonic acid impregnated montmorillonite K-10 (1:1 w/w) (*Scheme 52*).[61]

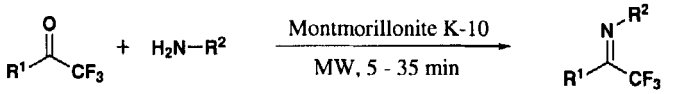
Microwave-assisted solvent-free synthesis of trifluoromethylated imines by montmorillonite K-10 catalyzed condensation of α,α,α-trifluoromethyl ketones and amines were achieved recently. Despite the significantly deactivated nature of trifluoromenthylketones, the product imines were isolated in good to excellent yields in short times (*Scheme 53*).[62] In contrast, the traditional method (PTSA, toluene, reflux) gave 70% yield in seven days.

Maleic anhydrides and phthalic anhydrides underwent condensation with different diamines in the presence of montmorillonite K-10 or montmorillonite KSF under microwave irradiation to give different bismaleimides and bisphthalimides in good yield (*Scheme 54*).[63]



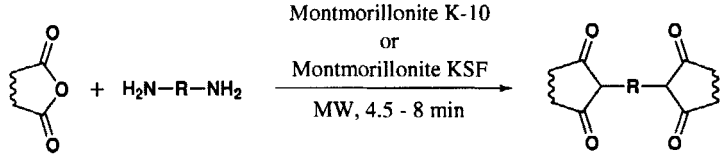


Scheme 52



R^1 = C_6H_5, $C_6H_5CH_2$, naphthyl, 2-pyrrolyl, 2-thiophenyl, 3-indolyl
R^2 = C_6H_5, $C_6H_5CH_2$, 2-naphthyl, 2-$NH_2C_6H_4$, 2-$NH_2C_6H_4CH_2$, 2-$CH_3C_6H_4$, 4-$CH_3C_6H_4$, 3-$CF_3C_6H_4$, 4-ClC_6H_4, 4-FC_6H_4, $C_6H_5CH(CH_3)$

Scheme 53



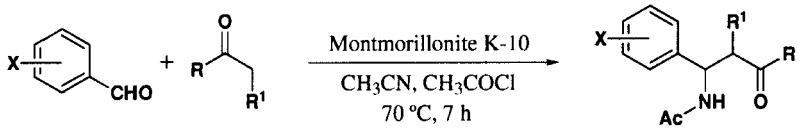
Maleic anhydride, phthalic anhydride, 4-chlorophthalic anhydride, 3,6-dichlorophthalic anhydride — 60 - 89%

R = -$(CH_2)_2$-, -$(CH_2)_6$-, -C_6H_4(1,4)-, -C_6H_4(1,4)-C_6H_4(1,4)-, -C_6H_4(1,4)-CH_2-C_6H_4(1,4)-, -C_6H_4(1,3)-, -C_6H_4(1,4)-O-C_6H_4(1,4)-

Scheme 54

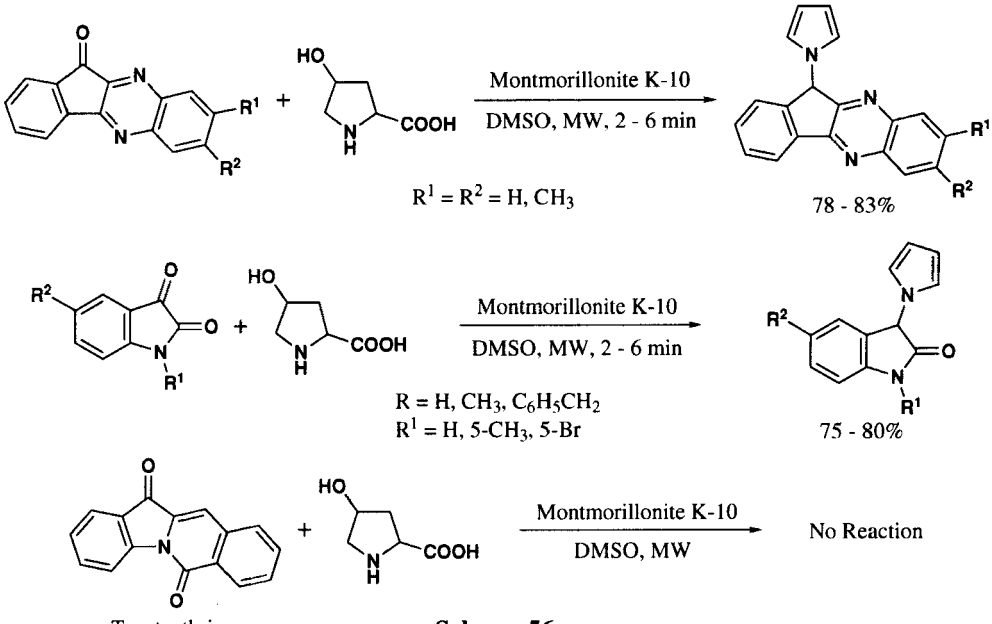
A highly stereoselective synthesis of β-acetamido ketones was carried out with montmorillonite K-10 in a one-pot three-component coupling reaction of aldehyde, ketone and acetonitrile in the presence of acetyl chloride. The reaction provided moderate yields under mild conditions (*Scheme 55*).[64]

The condensation of 11*H*-indeno[1,2-*b*]quinoxalin-11-one or isatin derivatives with 4-hydroxyproline in the presence of montmorillonite K-10 under microwave irradiation afforded 11H-(1*H*-pyrrol-1-yl)-11*H*-indeno[1,2-*b*]quinoxalines and 3-(1*H*-pyrrol-1-yl)indolin-2-one derivatives in good yields, although tryptanthrine did not react under these conditions (*Scheme 56*).[65]



X = H, 2-OH, 4-NO_2, 3-NO_2, 2-NO_2, 4-CN, 2-Cl, 4-COOH, 4-CH_3
R = C_6H_5, CH_3; R^1 = H, CH_3; R-R^1 = cyclohexane

Scheme 55



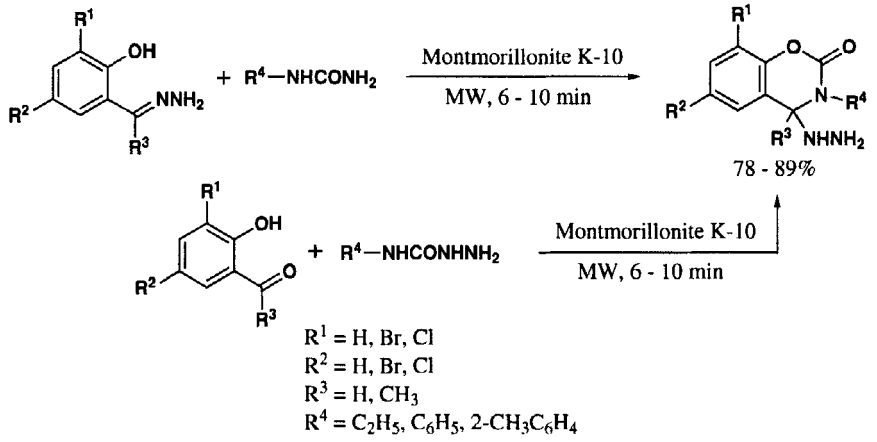
Scheme 56

The condensation of aryl- or alkylureas with hydrazones of salicylaldehyde or 2-hydroxyacetophenone, or the condensation of 4-aryl- or 4-alkylsemicarbazides with salicylaldehydes or 2-hydroxyacetophenones readily occurred in a one-pot reaction. The reaction was catalyzed by montmorillonite K-10 under microwave conditions, and provided a variety of 3,4-dihydro-4-hydrazino-2*H*-benz[*e*]-1,3-oxazin-2-ones (*Scheme 57*).[66]

2,2-Dimethylbenzopyran derivatives were prepared by the condensation of substituted phenols with prenyl bromide in the presence of montmorillonite K-10 as catalyst in carbon tetrachloride (*Scheme 58*).[67]

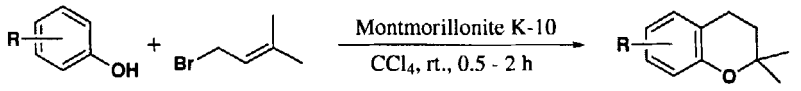
K^+-ion-exchanged montmorillonite K-10 was used to catalyze the condensation of various phenols with 3-methyl-2-butenal under microwave conditions to give substituted chromenes (*Scheme 59*).[68]

Sesamol was condensed with 3-methyl-2-butenal under similar conditions to afford methylenedioxyprecocene, an insecticide, which exhibits anti-juvenile hormone activity in some insects (*Scheme 60*).[68]



R^1 = H, Br, Cl
R^2 = H, Br, Cl
R^3 = H, CH_3
R^4 = C_2H_5, C_6H_5, 2-$CH_3C_6H_4$

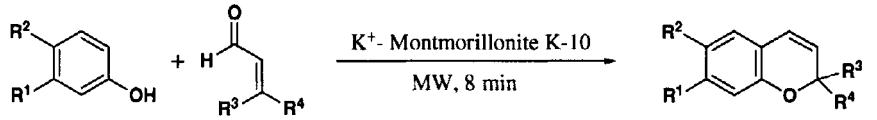
Scheme 57



40 - 100%

R = H, 3,4-(OCH_2O), 3,4-($CH_3O)_2$, 4-CH_3O, 3-CH_3, 4-CH_3, 4-CH_3CO, 3-HO

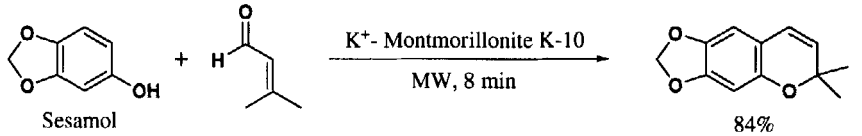
Scheme 58



10 - 50%

R^1 = CH_3O; R^2 = CH_3O; R^1, R^2 = -$O(CH_2)O$-
R^3 = H, CH_3; R^4 = H, CH_3

Scheme 59



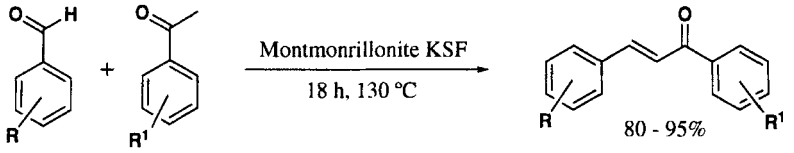
Sesamol

84%
Methylenedioxy precocene

Scheme 60

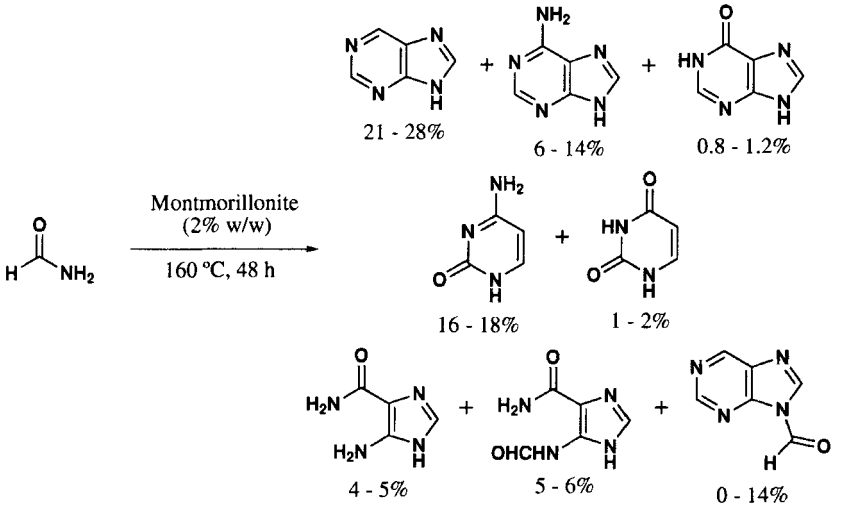
Montmorillonite KSF was used as a reusable solid acid catalyst for the condensation of aldehydes with acetophenones to give *trans*-chalcones in high yields and selectivities (*Scheme 61*).[69]

Formamide in the presence of montmorillonites readily underwent self-condensation to produce a mixture of purine, adenine, cytosine, uracil, 5-aminoimidazole-4-carboxamide, 5-formamidoimidazole-4-carboxamide and hypoxanthrine (*Scheme 62*).[70]



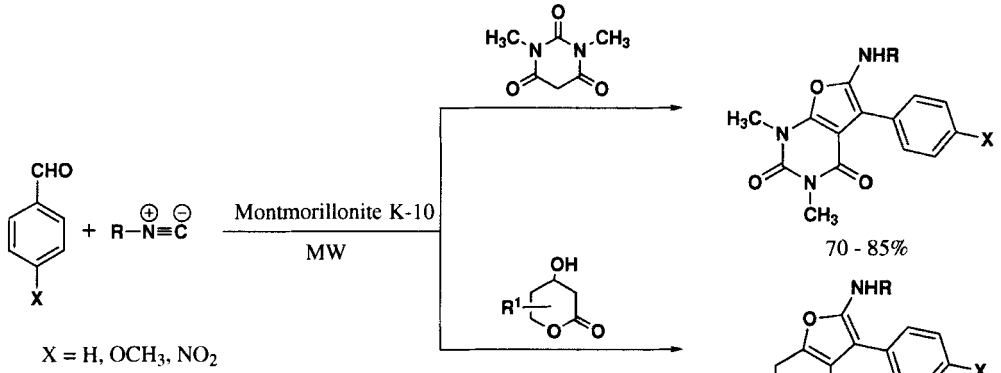
R = H, 4-Cl, 4-OCH_3, 2-Cl, 4-CN, 4-NO_2, 4-C_6H_5
R^1 = H, 4-CH_3, 4-Cl

Scheme 61



Scheme 62

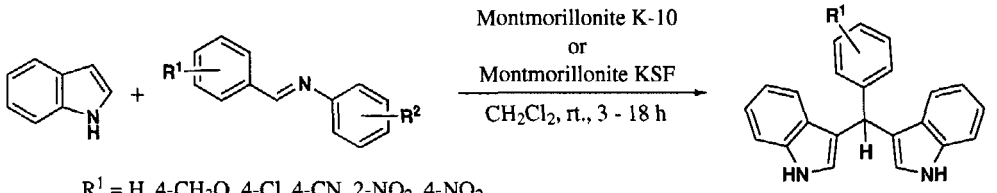
Furopyrimidines, furocoumarins and furopyrones were synthesized in the presence of montmorillonite K-10, under microwave conditions, by a one-pot three-component condensation reaction of *N,N'*-dimethyl barbituric acid or 4-hydroxy coumarins or 4-hydroxy pyrones with 4-substituted benzaldehydes and alkyl- or arylisocyanides. Furopyrimidines and furocoumarines are an important class of compounds exhibiting a wide range of biological activities (*Scheme 63*).[71]



X = H, OCH_3, NO_2
R = cyclohexyl, $(CH_3)_3C$, 2,6-dimethylphenyl
R^1 = 4-hydroxycoumarin, 4-hydroxy-6-methyl pyrone

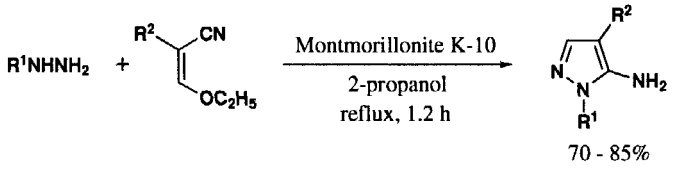
Scheme 63

Chemoselective condensation of indoles and imines were carried out in the presence of montmorillonite K-10 or montmorillonite KSF at room temperature to give diindolyl aryl-methanes (*Scheme 64*).[72]



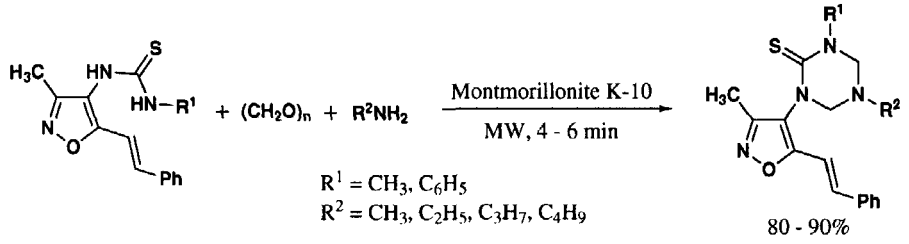
Scheme 64

Montmorillonite K-10 was used as catalysts for the condensation of phenylhydrazines with ethoxymethylene cyanoacetate or ethoxymethylene malononitrile under reflux conditions in propan-2-ol to give 5-aminopyrazolecarboxylates and nitriles in good yields (*Scheme 65*).[73]



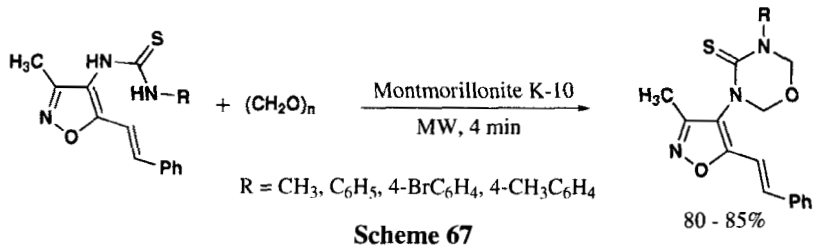
Scheme 65

Isoxazolyl triazinethiones were synthesized in high yields, by trimolecular condensation of *N*-(3-methyl-5-styryl-isoxazol-4-yl)-*N'*-aryl thioureas, paraformaldehyde and primary amines in the presence of montmorillonite K-10 under microwave-assisted conditions (*Scheme 66*).[74]

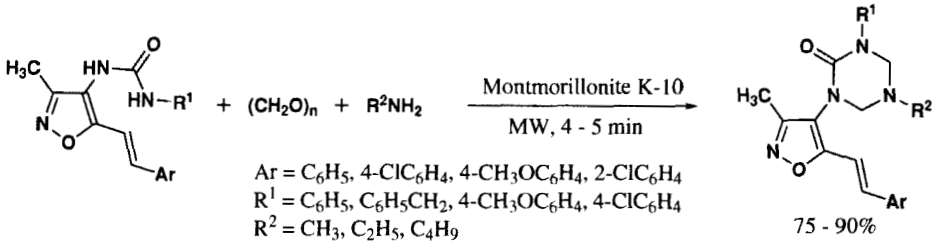


Scheme 66

Isoxazolyl oxadiazinethiones were obtained in excellent yields by the condensation of paraformaldehyde with *N*-(3-methyl-5-styryl-isoxazol-4-yl)-*N'*-aryl thioureas under similar conditions (*Scheme 67*).[74] This method was extended to the formation of isoxazolyl-[1,3,5]-triaz-inan-2-ones by the condensation of *N*-(3-methy-5-styryl-4-isoxazolyl)-*N'*-aryl ureas, paraformaldehyde and primary amines in the presence of montmorillonite K-10 using microwave activation (*Scheme 68*).[75]

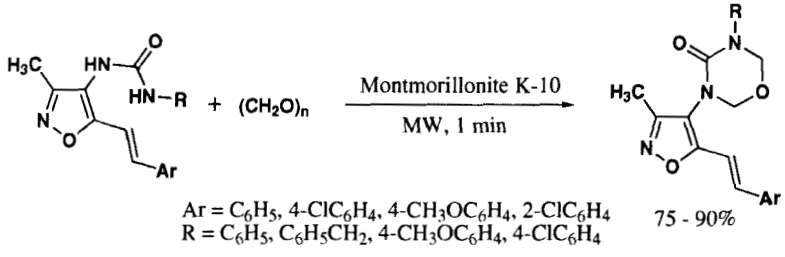


Scheme 67



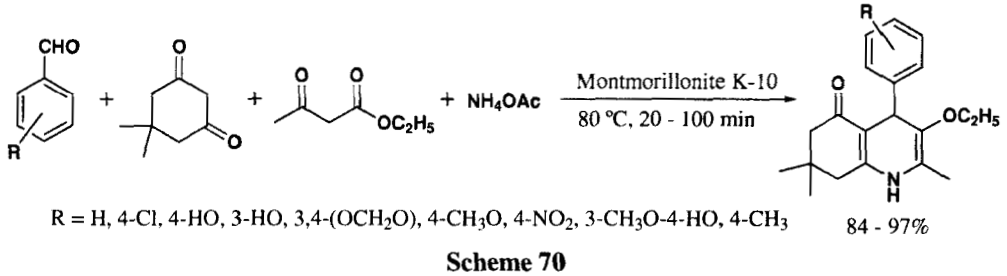
Scheme 68

The synthesis of isoxazolyl-[1,3,5]-oxadiazinan-4-ones was achieved by the condensation of *N*-(3-methy-5-styryl-4-isoxazolyl)-*N'*-aryl ureas with paraformaldehyde in the absence of primary amines in the presence of montmorillnite K-10 under microwave irradiation (*Scheme 69*).[75]



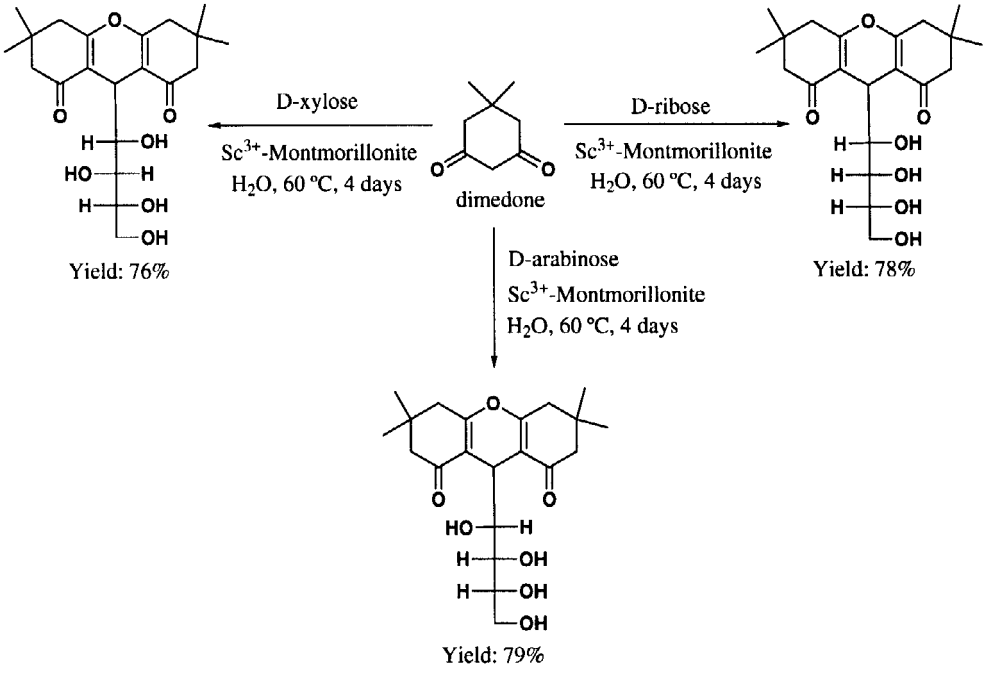
Scheme 69

Polyhydroquinoline derivatives were prepared efficiently by a four component coupling reaction involving aromatic aldehydes, dimedone, ethyl acetoacetate and ammonium acetate in the presence of montmorillonite K-10 at 80 °C. The yields were around 90% and the clay could be reused several times (*Scheme 70*).[76]



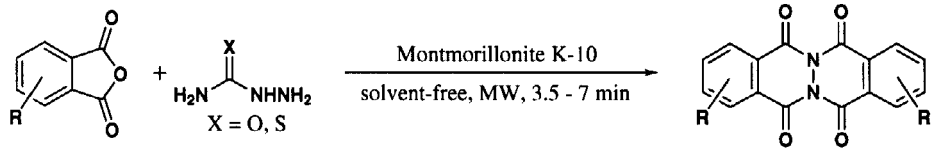
Scheme 70

Catalytic amount of Sc^{3+}-montmorillonite was used for the condensation of dimedone with unprotected carbohydrates to give 9-hydroxyalkyl-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-1*H*-xanthane-1,8-(2*H*)-diones in good yields (*Scheme 71*).[77] The catalyst could be recycled several times without deactivation.



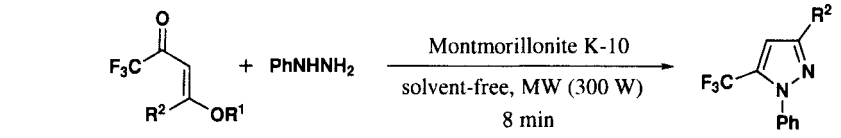
Scheme 71

Phthalazino[2,3-*b*]phthalazine-5,7,12,14-tetrones were synthesized by the condensation of semicarbazide or thiosemicarbazide with various phthalic anhydrides in the presence of montmorillonite K-10 under solvent-free conditions and under microwave irradiation (*Scheme 72*). The montmorillonite K-10 could be recycled.[78]

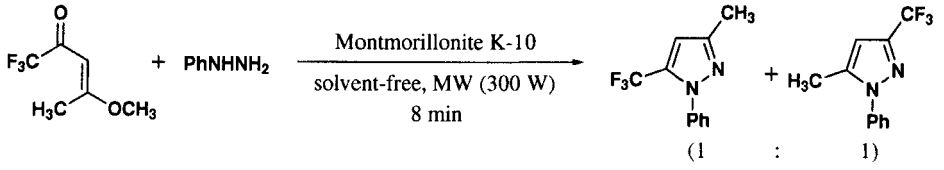


Scheme 72

The condensation of 4-alkoxy-4-alkyl-1,1,1-trifluoro-3-alken-2-ones with phenylhydrazine to synthesize 5-trifluoromethyl-1-phenyl pyrazoles were carried out using montmorillonite K-10 as the solid support under solvent-free conditions and under microwave irradiation (*Scheme 73*).[79]



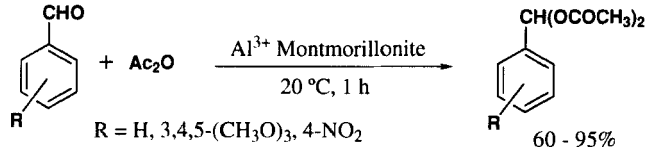
$R^1 = CH_3, C_2H_5$
$R^2 = H, CH_3, C_2H_5, C_3H_7, (CH_3)_2CH, C_4H_9, (CH_3)_3C, C_6H_5$



Scheme 73

6. Protection-Deprotection Reactions

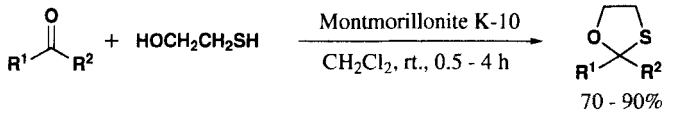
Metal cation-exchanged montmorillonites were used as catalysts for the protection of aromatic aldehydes with acetic anhydride. Al^{3+}-ion exchanged montmorillonite showed the best catalytic performance, giving moderate to good yields (*Scheme 74*).[80]



R = H, 3,4,5-$(CH_3O)_3$, 4-NO_2

Scheme 74

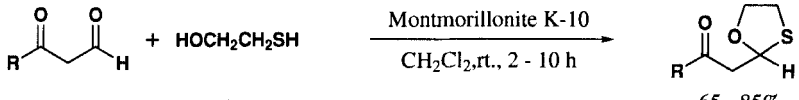
Various carbonyl compounds were protected as the corresponding oxathiolanes with 2-mercaptoethanol in the presence of montmorillonite K-10 at room temperature (*Scheme 75*).[81]



$R^1 = C_6H_5$, 2,3,4-$(CH_3O)_3C_6H_2$, $CH_3CH{=}CH$, C_2H_5, 4-$CH_3OC_6H_4$, 4-HOC_6H_4, $C_6H_5CH{=}CH$, 2-furyl
R^2 = H; R^1, R^2 = cyclohexyl, cycloheptyl, 6-methoxy-1-tetralone

Scheme 75

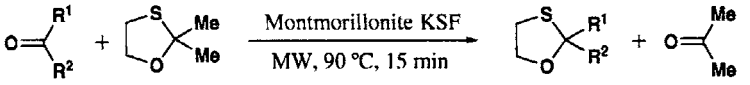
This method was extended to the chemoselective protection of the aldehyde functionality in the presence of β-keto-functional group (*Scheme 76*).[79]



R = C_6H_5, $C_6H_5CH_2$, 4-ClC_6H_4, 4-$CH_3OC_6H_4$, $CH_3C_6H_4$, 4-$O_2NC_6H_4$, 2-thiophenyl, 2-furyl

Scheme 76

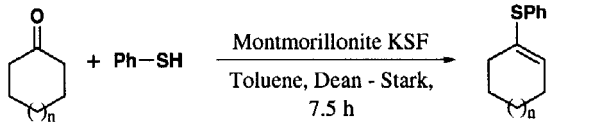
Aldehydes and ketones were converted to the corresponding oxathiolanes under microwave irradiation and solvent-free conditions in the presence of montmorillonite KSF (*Scheme 77*).[82]



$R^1 = C_6H_5CH_2$, $C_6H_5CH_2CH_2$, $C_6H_5(CH_3)CH$, C_6H_5, $CH_3CH{=}CH$, $(CH_3)_2CHCH_2$
$R^2 = H$, CH_3
$R^1, R^2 = C_5H_{10}$

Scheme 77

Montmorillonite KSF was used as an efficient catalyst for the synthesis of enol thioethers from the respective cyclic ketone precursors. The phenyl vinyl sulfides were obtained from the cyclic ketones in very good yields (*Scheme 78*).[83]

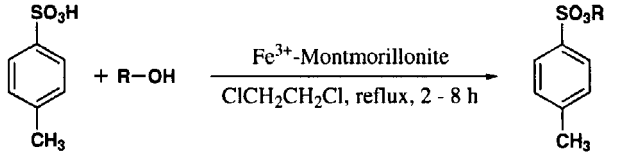


n = 1, 2

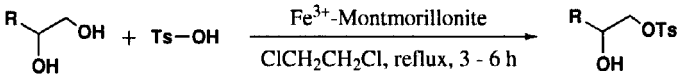
n = 1 88%
n = 2 86%

Scheme 78

The tosylation of alcohols and selective monotosylation of diols were achieved by an enviro-economic route using 4-toluenesulfonic acid along with Fe^{3+}-exchanged montmorillonite. Primary hydroxy groups undergo tosylation selectively in the presence of both primary and secondary hydroxy groups (*Scheme 79*).[84]



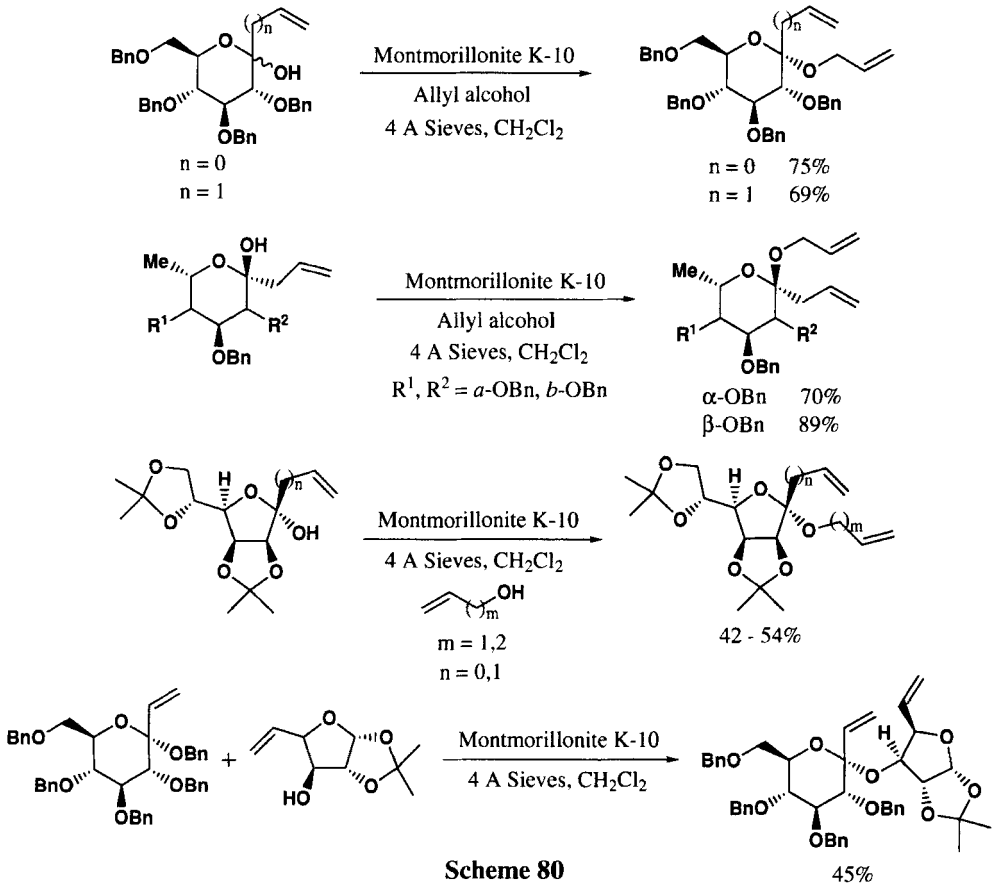
R = CH_3, C_2H_5, C_5H_{11}, $(CH_3)_2CH$, cyclopentyl, cyclohexanyl, allyl, etc.



R = CH_3, $(CH_3)_3C$, $ClCH_2$, etc.

Scheme 79

Montmorillonite K-10 was used for glycosidations with allyl alcohol to yield the corresponding pure α-ketoglycoside isomers. The reaction of different alkenols with various carbohydrate derivatives was studied. The method was further extended to the glycosidation of vinylketoses with the isopropylidene acceptor, derived from the carbohydrate (*Scheme 80*).[85]

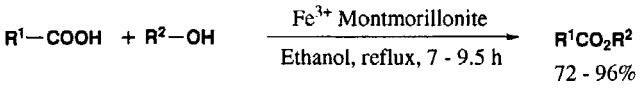


Scheme 80

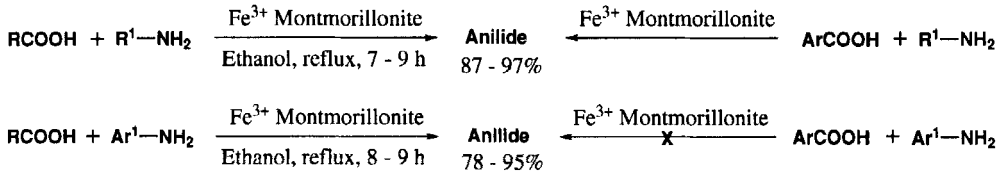
Aliphatic carboxylic acids were selectively esterified in the presence of aromatic carboxylic acids by Fe^{3+}-exchanged montmorillonite K-10. Aliphatic amines formed the corresponding amides from both aliphatic and aromatic carboxylic acids, but aromatic carboxylic acids failed to generate anilides with aromatic amines using Fe^{3+}-exchanged montmorillonite K-10 catalysis (*Scheme 81*).[86]

Montmorillonite K-10 was used to selectively regenerate carboxylic acids from the corresponding substituted allyl esters, under microwave accelerated solvent-free conditions, in higher yields than those obtained under thermal conditions (using toluene as a solvent). The aryl and alkyl esters remained unaffected, while cinnamyl ester required the presence of a more nucleophilic aromatic species like anisole for regeneration of the acid (*Scheme 82*).[87]

Phenols containing acetal-type protecting groups, like methoxymethyl (MOM), methoxyethoxymethyl (MEM), or trimethylsilylethoxymethyl (SEM) groups, and having an *ortho* heteroatom substitution were efficiently deprotected in the presence of montmorillonite K-10 at room temperature. The selectively deprotected allyl-naphthol was also isolated in 95% yield after the cleavage of MOM-protected allyl-naphthol at room temperature in the presence of montmorillonite K-10 (*Scheme 83*).[88]

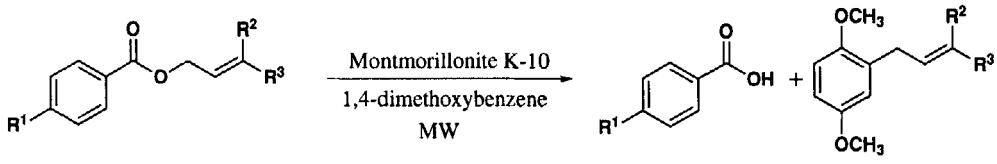


$R^1 = C_6H_5CH_2$, 4-$(OH)C_6H_4CH_2$, 3,4-$(OH)_2C_6H_3CH_2$, $CH_3(CH_2)_{16}$, $CH_3(CH_2)_7CH{=}CH(CH_2)_7$, PhCH=CH, CH_3CO, 2-$(COOH)C_6H_4CH_2$, 2-$(COOH)C_6H_4CH_2CH_2$
$R^2 = CH_3$, C_2H_5, $(CH_3)_2CH$, $C_6H_5CH_2$



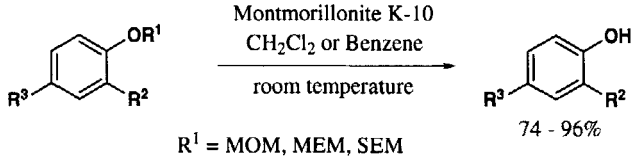
R, R^1 = Alkyl; Ar, Ar^1 = Aryl

R = $C_6H_5CH_2$, 4-$(HO)C_6H_4CH_2$, 3,4-$(HO)_2C_6H_3CH_2$, C_2H_5, $C_6H_5CH{=}CH$, 2-$(COOH)C_6H_4CH_2CH_2$
R^1 = $C_6H_5CH_2$, 4-$(CH_3O)C_6H_4CH_2$, $C_6H_5CH_2CH_2$
Ar = C_6H_5, 4-$(HO)C_6H_4$
Ar^1 = C_6H_5, 4-$(CH_3O)C_6H_4$, 4-ClC_6H_4 **Scheme 81**

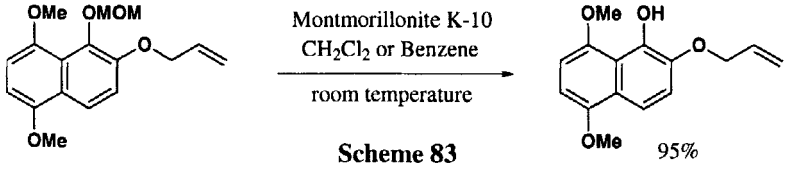


R^1 = H, CH_3, OCH_3, NO_2, Cl
R^2, R^3 = H, CH_3, C_6H_5

Scheme 82

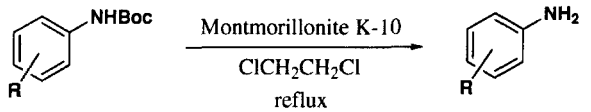


R^1 = MOM, MEM, SEM
R^2 = NO_2, OCH_3, CHO, $COOCH_3$
R^3 = H, CHO, OMOM, NO_2, OCH_3

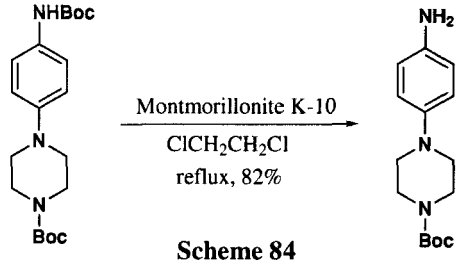


Scheme 83

Montmorillonite K-10 readily removed the protecting group from *tert*-butoxycarbonyl protected aromatic amines when heated under reflux in dichloroethane. The reaction was selective for aromatic amines, the *tert*-butoxycarbonyl protected aliphatic amines remaining unchanged (*Scheme 84*).[89]

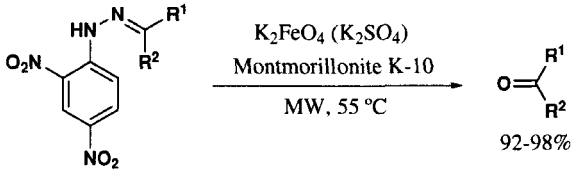


R = H, 4-Cl, 4-NO_2, 4-CH_3, 4-OCH_3, 2-OH, 4-$C(OCH_2CH_2O)CH_3$



Scheme 84

Potassium ferrate(VI) supported on montmorillonite K-10 was used to regenerate carbonyl compounds from the corresponding 2,4-dinitrophenylhydrazones under microwave irradiation in very high yields (*Scheme 85*).[90]



R^1 = C_6H_5, 4-$CH_3C_6H_4$, 4-$CH_3OC_6H_4$, 3-$NO_2C_6H_4$, 4-C_6H_4, $C_6H_5CH{=}CH$, C_7H_{15}, 2-ClC_6H_4, ClC_6H_4, 2-BrC_6H_4, 4-BrC_6H_4
R^2 = H, CH_3, C_6H_5
R^1, R^2 = -$(CH_2)_5$-

Scheme 85

Chemoselective cleavage of *tert*-butyl esters was achieved in the presence of other protecting functional groups such as Boc, Cbz, propargyl, allyl, etc., in high yields with montmorillonite KSF in acetonitrile under reflux conditions (*Scheme 86*).[91]

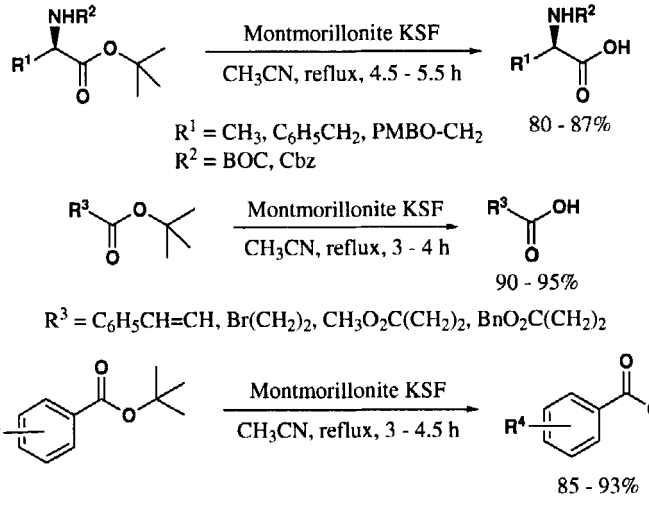
7. Rearrangements and Isomerizations

Montmorillonite K-10 was used under solvent-free microwave conditions for the isomerization of various acetates of Baylis-Hillman adducts and unsaturated alcohols in the presence of trimethyl orthoformate, to provide trisubstituted *(E)*-alkenes in high yields (*Scheme 87*).[92]

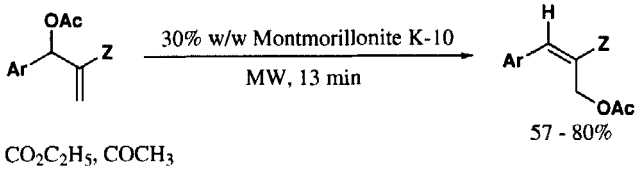
This procedure was extended to the synthesis of substituted tetrahydrofurans, which form the core structure of various lignans (*Scheme 88*).[92]

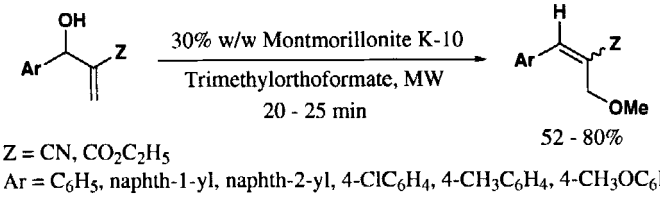
Montmorillonite K-10 was used as a catalyst for the cyclo-isomerisation of salicylaldehyde 4-(β-D-ribo or β-D-2'-deoxyribofuranosyl)-semicarbazones to benzoxazinone nucleosides, 4-hydrazino-3,4-dihydro-3-(*β*-D-ribo- or *β*-D-2'-deoxyribofuranosyl)-2*H*-benz-[*e*]-1,3-oxazin-2-

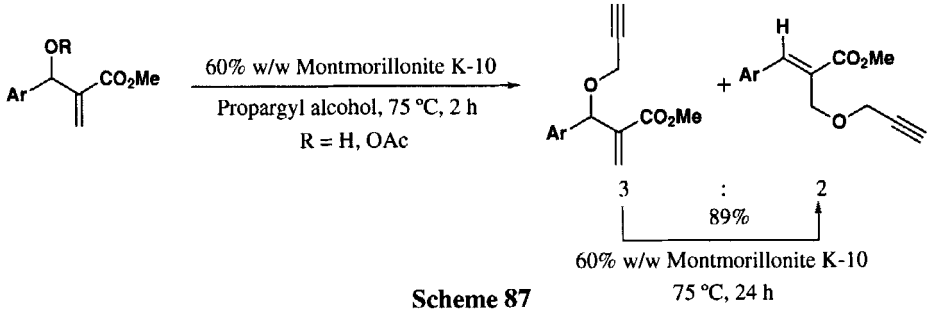
ones. Benzoxazinones have recently been identified as non-nucleoside reverse transcriptase inhibitors and are thus pharmaceutically important (*Scheme 89*).[93]



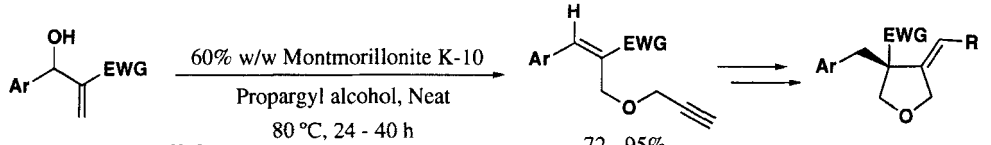
Scheme 86







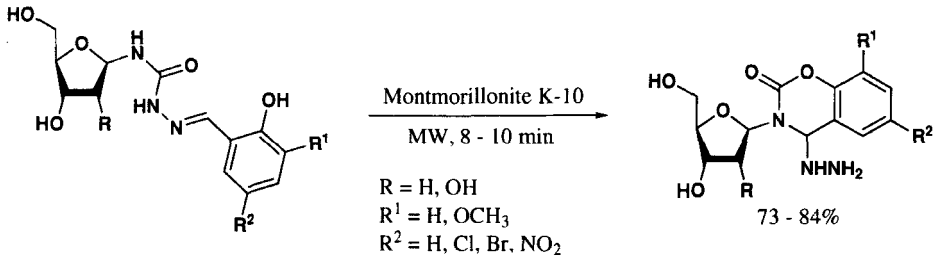
Scheme 87



72 - 95%

R = H, I
EWG = CN, $CO_2C_2H_5$, CO_2CH_3
Ar = C_6H_5, 4-ClC_6H_4, 4-$CH_3C_6H_4$, 4-$CH_3OC_6H_4$

Scheme 88

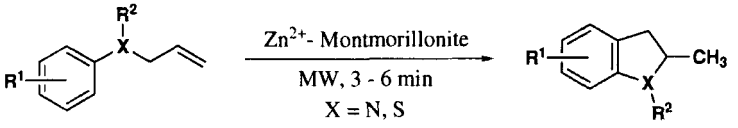


R = H, OH
R^1 = H, OCH_3
R^2 = H, Cl, Br, NO_2

73 - 84%

Scheme 89

Zn^{2+}-Exchanged montmorillonite was used to catalyze the 3-*aza*-Cope rearrangement of *N*-alkylanilines under microwave irradiation to give indoline derivatives in high yields (*Scheme 90*).[94]

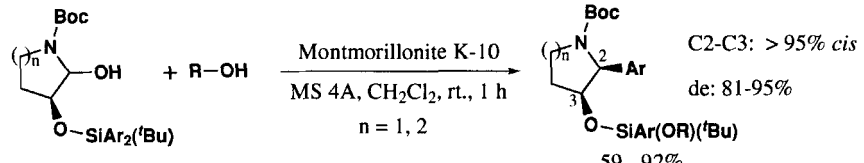


70 - 85%

R^1 = H, CH_3O, 4-F, 4-CH_3O, 4-CN, 4-NO_2, 2-naphthyl
R^2 = H, $C_6H_5CH_2$, CH_3, C_2H_5

Scheme 90

Montmorillonite K-10 was used in the presence of molecular sieves to induce a novel 1,4-aryl migration from silicon to carbon in β-*tert*-butyldiarylsiloxypyrrolidine or piperidine hemiaminals in a highly stereoselective manner. The product α-aryl-β-hydroxy cyclic amines are important synthetic building blocks, and are difficult to obtain by other methods (*Scheme 91*).[95]



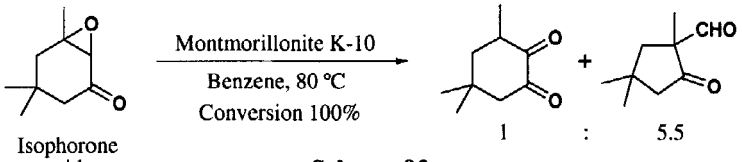
C2-C3: > 95% *cis*
de: 81-95%

R = $C_6H_5CH_2$, CH_2=CH-CH_2, CH_2-C≡ CTMS, CH_3
Ar = C_6H_5, 4-$CH_3C_6H_4$

59 - 92%

Scheme 91

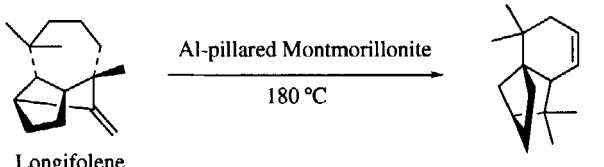
Montmorillonite K-10 catalyzed the formation of α-formylketones or *vic*-diones *via* the rearrangement of various cyclic α,β-epoxy ketones, which appears to be an attractive synthetic methodology. The yields and selectivities were good and the catalyst could be recovered and recycled (*Scheme 92*).[96]



Isophorone oxide

Scheme 92

Al-pillared montmorillonite was an efficient catalyst for the rearrangement of *longifolene* to isolongifolene (*Scheme 93*).[97]

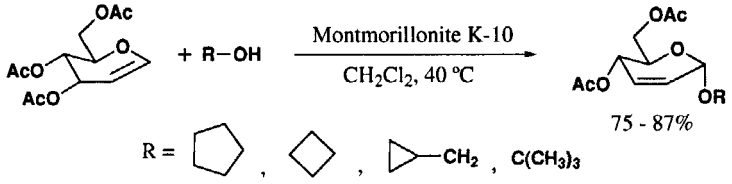


Longifolene

Isolongifolene
77%

Scheme 93

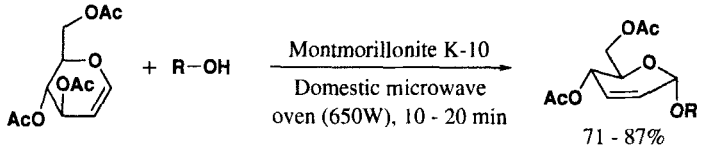
2,3-Unsaturated glycosides are versatile chiral synthetic intermediates and are usually prepared by the acid-catalyzed rearrangement of glycals in the presence of alcohols, also known as the Ferrier rearrangement. Montmorillonite K-10 was used as a Lewis acid for the glycosidation of 3,4,6-tri-*O*-acetyl D-glucal with different alcohols to give unsaturated glycosides (*Scheme 94*).[98] This procedure was extended for the synthesis of different amino carbohydrate



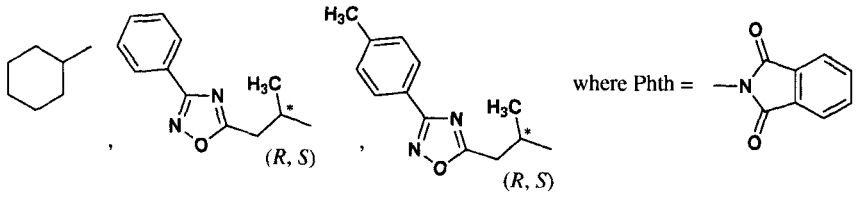
Scheme 94

precursors.[99] The same reaction was carried out in the presence of montmorillonite K-10 under microwave conditions to initiate the allylic rearrangement of tri-*O*-acetyl-D-glucal with alcohol to unsaturated glycosides. This was the first application of microwave irradiation to carry out Ferrier rearrangement (*Scheme 95*).[100]

The Ferrier rearrangement in the presence of montmorillonite K-10 was further extended

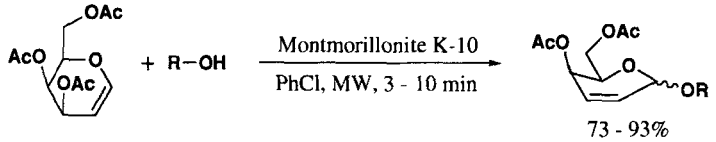


R = Phth-CH_2-, Phth-CH_2CH_2-, (*S*)-(+)-Phth-$CH(CH_3)CH_2$-



Scheme 95

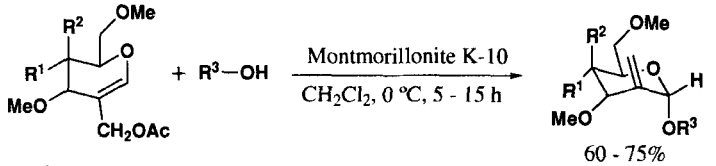
under microwave irradiation to the glycosidation of 3,4,6-tri-*O*-acetyl-D-galactal (*Scheme 96*).[101]



R = CH_3CH_2, $C_6H_5CH_2$, C_6H_{11}, $HC{\equiv}CCH_2$, $CH_2{=}CH\text{-}CH_2$, C_6H_5, 4-$CH_3OC_6H_4$, 4-ClC_6H_4, 4-$CH_3C_6H_4$, 3,4-$(CH_3)_2C_6H_3$

Scheme 96

The rearrangement for the glycosylation of allyl acetates with various alcohols were also carried out at room temperature in the presence of montmorillonite K-10 (*Scheme 97*).[102]

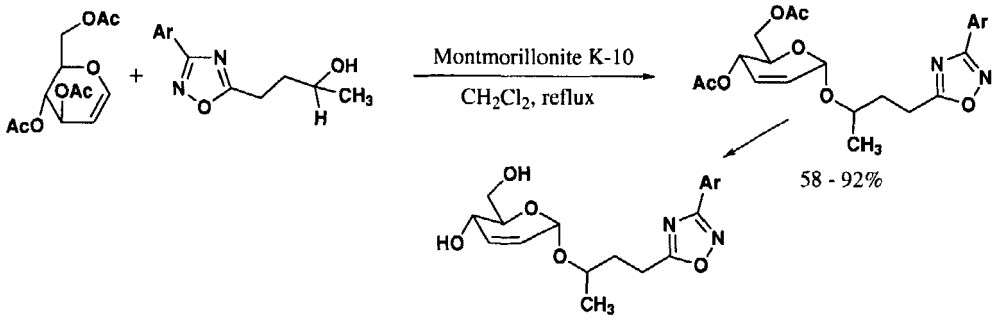


R^1 = H, OCH_3
R^2 = H, OCH_3
R^3 = $C_6H_5CH_2$, 4-$CH_3C_6H_4$, $(CH_3)_3C$, cyclohexyl, allyl, β-naphthyl, etc.

Scheme 97

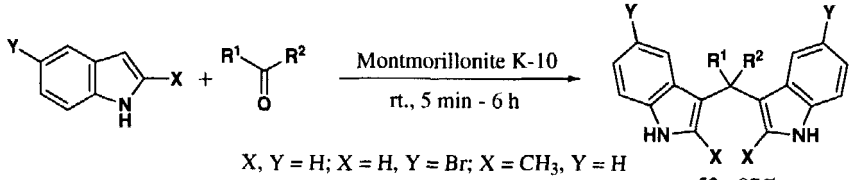
The Ferrier rearrangement of *racemic* 4-[3-(aryl)-1,2,4-oxadoazol-5-yl]-2-butanols with tri-*O*-acetyl-D-glucal was also catalyzed by montmorillonite K-10. Basic hydrolysis of the diastereomeric mixture gave the unsaturated glycosides (*R* or *S*)-1-methyl-3-[3-(aryl)-1,2,4-oxadiazol-5-yl]-propyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranosides, with a stereocenter present in the aglycone moiety as well (*Scheme 98*).[103]

3,3'-Diindolylalkanes were formed by the reaction of indole or 2- or 5-substituted indoles on montmorillonite K-10 at room temperature with different aldehydes, ketones and acetals (*Scheme 99*).[104]



Ar = C_6H_5, 2-$CH_3C_6H_4$, 3-$CH_3C_6H_4$, 4-$CH_3C_6H_4$, 4-ClC_6H_4

Scheme 98



X, Y = H; X = H, Y = Br; X = CH_3, Y = H

52 - 97%

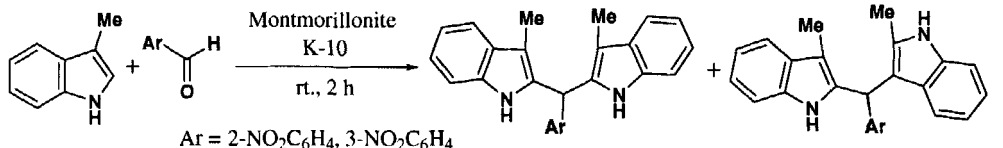
R^1 = CH_3, C_2H_5, C_6H_5, 2-$NO_2C_6H_4$, 3-$NO_2C_6H_4$, 4-$CH_3OC_6H_4$, 2-HOC_6H_4, 2-thiophenyl, 2-furyl

R^2 = H, CH_3

R^1, R^2 = cyclopentyl, cyclohexyl, 4-methylcyclohexyl, etc.

Scheme 99

When this method was performed with 3-methylindole (skatole) and 2- and 3- nitrobenzaldehyde, a Plancher rearrangement was observed (*Scheme 100*).[104]



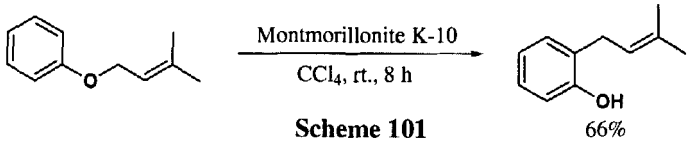
Ar = 2-$NO_2C_6H_4$, 3-$NO_2C_6H_4$

63%

27%

Scheme 100

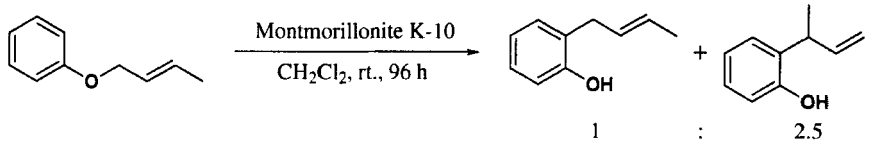
2-Prenylated phenols are important compounds, which show a wide range of pharmacological activities. 3-Methyl-2-butenyl phenyl ether underwent an *ortho*-Claisen-rerrangement in the presence of montmorillonite K-10, with high 2-selectivity in carbon-tetrachloride at room temperature to give 2-prenyl phenol (*Scheme 101*).[105]



Scheme 101

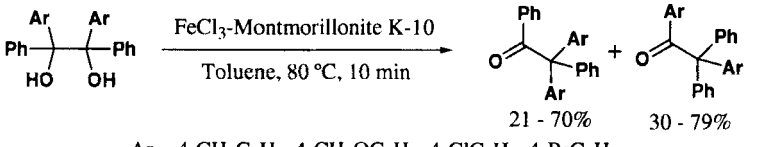
66%

If crotyl phenyl ethers were used as starting material in the above reaction, a competing [3,3]-rearrangement occurred along with the [1,3]-rearrangement, in the presence of montmorillonite K-10 in dichloromethane at room temperature (*Scheme 102*). The yields, however, were low compared to the prenyl ethers.[105]



Scheme 102

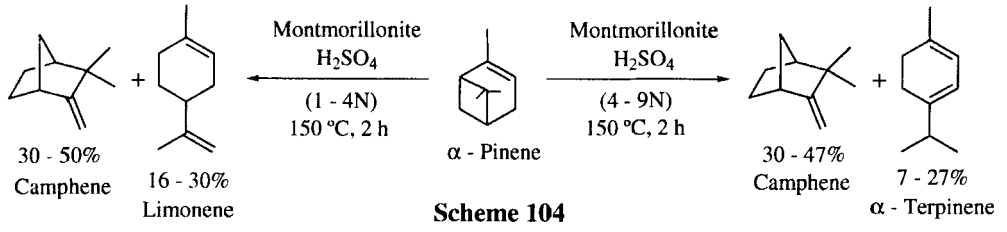
The pinacol-pinacolone rearrangement is an excellent method to synthesize highly branched ketones from *vic*-diols. Montmorillonite K-10 treated with anhydrous ferric chloride in acetonitrile is an excellent catalyst for the pinacol rearrangement of different symmetrical benzopinacols. The catalyst could be reused without any significant loss of activity (*Scheme 103*).[106]



Ar = 4-$CH_3C_6H_4$, 4-$CH_3OC_6H_4$, 4-ClC_6H_4, 4-BrC_6H_4

Scheme 103

The catalytic isomerization of α-pinene in the presence of natural Indian montmorillonite treated with sulfuric acid yielded camphene as the major product. The reaction appeared to be sensitive to the catalyst pre-treatment method. When the clay was treated with relatively dilute sulfuric acid (1-4 N H_2SO_4), limonene formed along with camphene (*Scheme 104*). When the

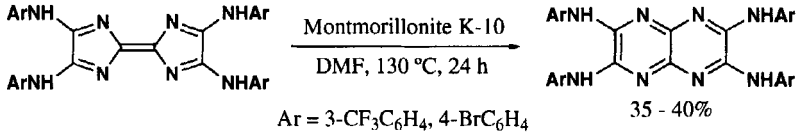


Scheme 104

clay was treated with more concentrated acid (5-9 N), however, the side-reaction gave α-terpinene. Montmorillonite clay exchanged with Ce^{3+} (camphene: 49%, limonene: 12%, α-terpinene: 8%), Fe^{3+} (camphene: 48%, limonene: 11%, α-terpinene: 8%), La^{3+} (camphene: 47%, limonene: 13%, α-terpinene: 9%) and Ag^{+} (camphene: 47%, limonene: 9%, α-terpinene: 11%) was also used for the isomerization to yield camphene as the major product.[107]

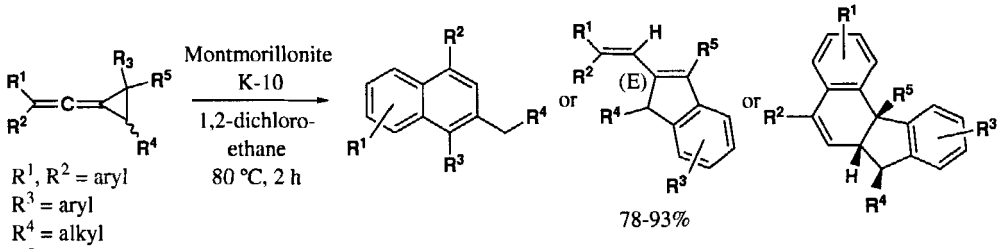
Tetraazafulvalenes undergo dyotropic rearrangements in the presence of montmoril-

lonite K-10 in boiling dimethylformamide (DMF) to give 1,4,5,8-tetraazanaphthalene compounds, which are otherwise difficult to synthesize (*Scheme 105*).[108]



Scheme 105

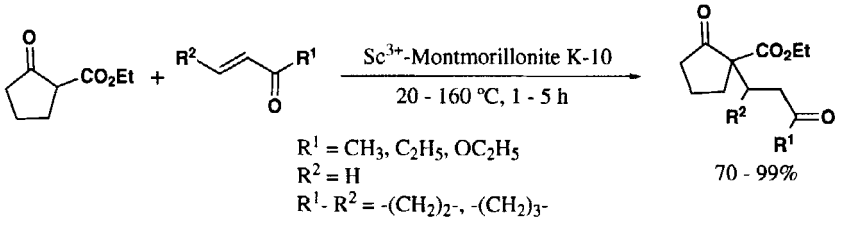
Several bicyclic aromatic compounds such as naphthalenes, indenes, and 6aH-benzo[c]fluorene derivatives were synthesized by an intramolecular rearrangement of substituted vinylidenecyclopropanes in the presence of montmorillonite K-10, under mild experimental reaction conditions in good to excellent yields. Depending on the selection of the R substituents, in particular the R^5 of the starting material three major products could be obtained selectively. The solid acidic catalyst, montmorillonite K-10, can be recycled after thorough washing and drying, although the number possible reuses or the activity of the catalyst after recovery were not discussed (*Scheme 106*).[109]



Scheme 106

8. Alkylation

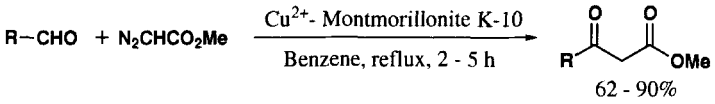
Sc^{3+} ion-exchanged montmorillonite K-10 efficiently catalyzed the Michael reaction of 1,3-dicarbonyl compounds with enones under solvent-free conditions. The catalyst was reusable without any appreciable loss of its high activity and selectivity (*Scheme 107*).[110]



Scheme 107

β-Ketoesters are important synthetic intermediates, and are used extensively in the agrochemical, pharmaceutical, and dye industries and are also utilized for the synthesis of natural products. Rh^{3+} and Cu^{2+} ion-exchanged montmorillonite K-10 catalyzed the reaction of methyl

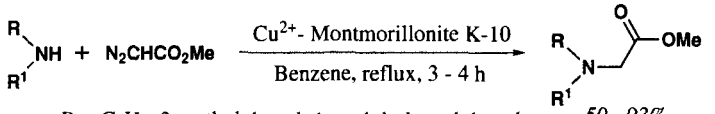
diazoacetate with various aldehydes to afford the corresponding β-ketoesters in high yield (*Scheme 108*).[111] The β-ketoesters obtained from aromatic aldehydes exist both as the *enol* and the *keto* forms.



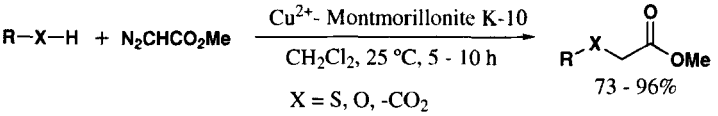
R = C_6H_5, 4-$CH_3OC_6H_4$, 3,4-$(CH_3O)_2C_6H_3$, 4-ClC_6H_4, C_9H_{19}, $(CH_3)_2CH$

Scheme 108

The metal ion-exchanged montmorillonite K-10 was also used to catalyze the insertion reaction of methyl diazoacetate into X-H bonds of amines, thiols, acids and alcohols (*Scheme 109*).[111]



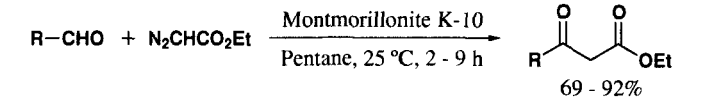
R = C_6H_5, 2-methylphenyl, 1-naphthyl, cyclohexyl
R^1 = H, CH_3, C_4H_9



X = S, O, $-CO_2$
R = Aryl, alkyl

Scheme 109

β-Ketoesters were synthesized efficiently by the modification of the above method, using pentane as a substitute for benzene. In this case, the reaction occurred at room temperature in the presence of montmorillonite K-10. The catalyst could be reused for three cycles without appreciable loss of activity (*Scheme 110*).[112]

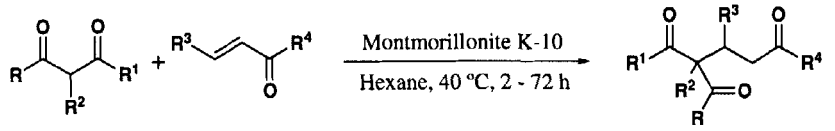


R = C_3H_7, C_5H_{11}, C_6H_5, 4-FC_6H_4, 4-ClC_6H_4, 4-CNC_6H_4, 4-$CH_3C_6H_4$, 4-$CH_3OC_6H_4$, 3,4-(-OCH_2O)-C_6H_3, C_6H_5CH=CH, 3-CH_3O-4-$COOCH_3C_6H_3$, 3,4,5-$(CH_3O)_3C_6H_2$, 4-$NO_2C_6H_4$

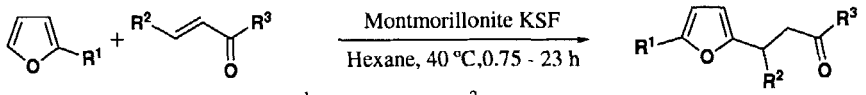
Scheme 110

The Michael addition and α-alkoxyalkylation of various 1,3-dicarbonyl compounds were carried out in the presence of montmorillonite K-10 and montmorillonite KSF (*Scheme 111*).[113]

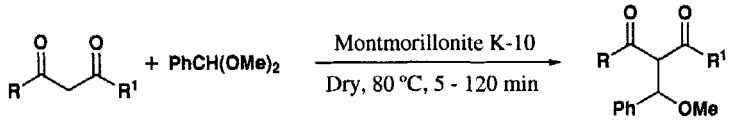
Stereoselective β-glycosidation of 2-iodo-olivosyl fluoride and alcohols to the corresponding 2-iodo-β-olivosides was achieved in high yields and high stereoselectivities using montmorillonite K-10 at room temperature (*Scheme 112*).[114]



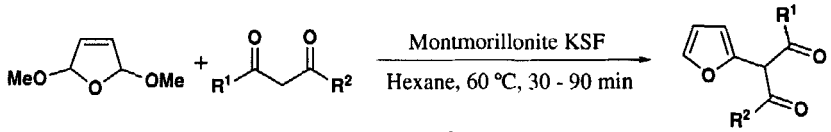
$R = C_6H_5, CH_3, OC_2H_5$; $R^1 = CH_3, OC_2H_5, CO_2Et$ 60 - 90%
$R^2 = H, CH_3$; $R^3 = H, CH_3$; $R^4 = CH_3$
$R^3, R^4 = -(CH_2)_3-$



$R^1 = CH_3, C_5H_{11}$; $R^2 = H, CH_3$ 42 - 86%
$R^3 = CH_3$; $R^2, R^3 = -(CH_2)_3-$

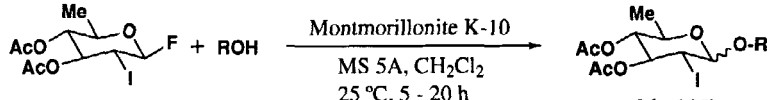


$R = C_6H_5, CH_3, (CH_3)_2CH$; $R^1 = OC_2H_5, CH_3, C_6H_5$ 42 - 86%



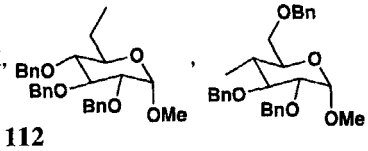
$R^1 = C_6H_5, CH_3, C_3H_7, (CH_3)_2CH$; $R^2 = OC_2H_5, CH_3, C_6H_5$ 66 - 74%

Scheme 111



86 - 98%
α:β = 8:92 - 19:81

$R = C_6H_{11}CH_2, C_8H_{17}$, cyclohexyl, $(CH_3)_2CH$,

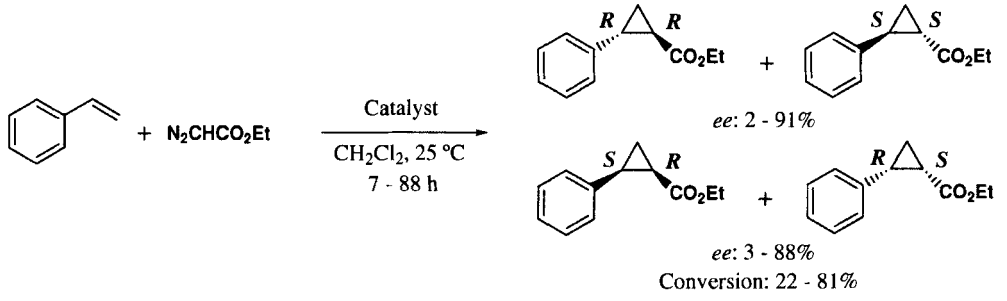


Scheme 112

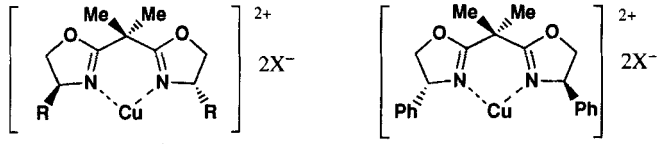
9. Cyclopropanation

Chiral *bis*(oxazoline)-copper complexes supported on laponite, bentonite and montmorillonite K-10 were used for cyclopropanation reaction of styrene with ethyl diazoacetate. Although, the reaction occurs on the acidic clay, the chiral ligand was used to initiate asymmetric cyclopropanation. Laponite was the support of choice for the reaction. The catalysts were reusable though a loss of activity and enantioselectivity were noted (*Scheme 113*).[115]

The cyclopropanation reaction was extended to chiral *bis*(oxazoline)-copper complexes supported on Nafion–silica nanocomposite. These catalysts were more effective than the laponite



Catalyst: Ligand-Cu(II)-Clay suport

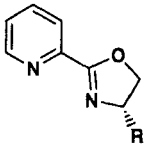


R = CH_2Ph, ^tBu X = Cl, TfO

Ligand

Scheme 113

supported sample. It gave 58% *ee* for *trans*-cyclopropanes and 47% *ee* for *cis*-cyclopropanes and the catalyst was reusable and showed stable catalytic performance over extended use.[116] The 2-[(*S*)-4-isopropyloxazolin-2-yl]pyridine-copper complex and 2-[(*S*)-4-phenyloxazolin-2-yl]pyridine-copper complex supported on laponite clay were excellent chiral catalysts and further improved the enantioselectivity (65% *ee*) of the cyclopropanation.[117a]

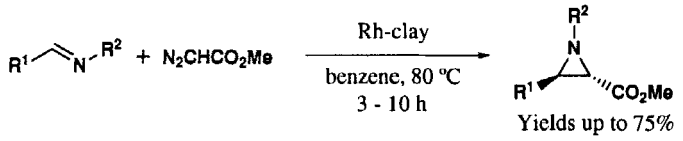


R = Ph: 2-[(*S*)-4-Phenyloxazolin-2-yl]pyridine
R = ^{i}Pr: 2-[(*S*)-4-Isopropyloxazolin-2-yl]pyridine

The mechanistic pathway for cyclopropanation was also studied and the reaction took place through nitrogen extrusion to form a copper-carbene complex, followed by a direct carbine insertion to the metal-carbene species to give a catalyst-product intermediate, which can regenerate the starting complex.[118] The heterogeneous catalyst gave better yields and enantiomeric excesses than the corresponding homogeneous alternative using the same catalyst.[117b]

10. Aziridination

A new heterogeneous catalytic synthesis of aziridines was described by a versatile carbenoid transfer to imines using several ion-exchanged clays as catalysts (*Scheme 114*).[119] Rh^{3+}- ion-exchanged K-10 montmorillonite provided the best yields in the exclusive formation of *trans* products.



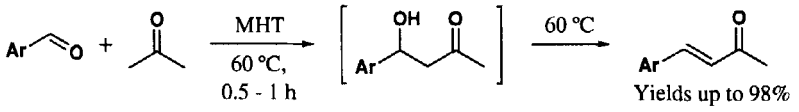
R^1= 4-ClC_6H_4, 4-$CH_3OC_6H_4$, 2-furyl, Bn, $(CH_3)_2CH$, etc.
R^2= C_6H_5, Cyclohexyl, 2,5-$Cl_2C_6H_3$, 3-NO_2-4-MeC_6H_3 etc.

Scheme 114

II. BASE CATALYSIS

1. Aldol Condensation

The aldol condensation between acetone and substituted benzaldehydes catalyzed by modified Mg-Al hydrotalcite (MHT) gave a wide variety of α,β-unsaturated methyl ketones (*Scheme 115*).[120] The reaction is limited to benzaldehydes having substituents, which lack acidic hydrogen. Phenol derivatives did not react at all or reacted very sluggishly. It is probably due to the acid-base interaction between the basic sites of the catalyst and the acidic hydroxyl group. As a result, the base strength of the catalyst diminished.

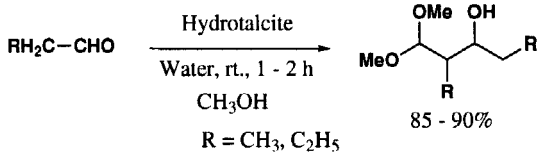


Ar = 4-NO_2-C_6H_4, 4-CH_3-C_6H_4, 4-CH_3O-C_6H_4, 3,4,5-$(CH_3O)_3$-C_6H_2, 4-Cl-C_6H_4 etc.

Scheme 115

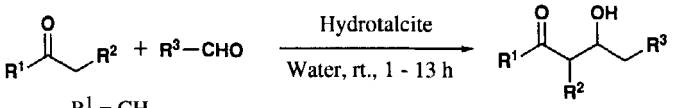
Reconstructed hydrotalcites efficiently catalyzed the aldol reaction of carbonyl compounds in the presence of water. The catalyst was reusable. In the presence of water, the hydroxyl ions present on the surface of the reconstructed hydrotalcite acted as Brønsted base sites to abstract hydrogen ions from the reactants (*Scheme 116*).[121]

Aldol Reaction



R = CH_3, C_2H_5

Cross-aldol Reaction

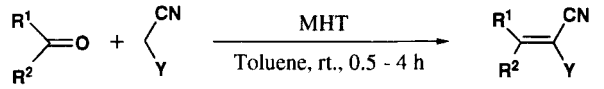


R^1 = CH_3
R^2 = H,
R^1, R^2 = cyclopentyl
R^3 = $(CH_3)_2CHCH_2$, $(CH_3)_2CH$, C_3H_7

Scheme 116

2. Knoevenagel Condensation

The Knoevenagel condensation between various carbonyl compounds and malononitrile and ethyl cyanoacetate was efficiently catalyzed by a modified Mg-Al hydrotalcite (MHT) catalyst (*Scheme 117*).[120]

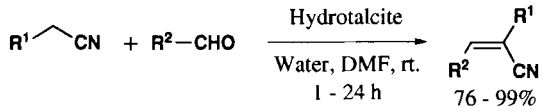


Yields 50 - 100%

R^1 = C_6H_5, C_6H_5CH=CH, 2-furyl, 3-furyl, 2-CH_3O-C_6H_4, 3-CH_3O-C_6H_4, 4-NO_2-C_6H_4 etc.
R^2 = H, CH_3
Y = CN, CO_2Et

Scheme 117

The Knoevenagel reaction between aldehydes and nitriles could be achieved in water in the presence of reconstructed hydrotalcite as a catalyst. The reconstructed hydrotalcite was an efficient heterogeneous catalyst for the formation of a carbon–carbon bond in the aqueous medium (*Scheme 118*).[121]



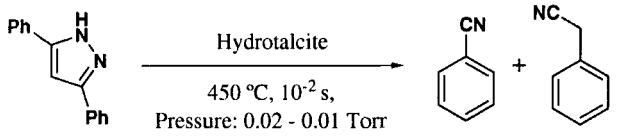
76 - 99%

R^1 = C_6H_5, H_2NCO, 2-pyridyl, CN, COOEt
R^2 = C_6H_5, 2-furyl, C_7H_{15}, cyclohexyl, $(CH_3)_2CH$,
$(CH_3)_2C$=$CHCH_2CH_2C(CH_3)$=CHCHO (*E* and *Z*), C_6H_5CH=CH

Scheme 118

3. Rearrangements

3,5-Diphenylpyrazole underwent fragmentation and rearrangement to nitriles at 450 °C in the presence of anionic clays having hydrotalcite structure. The yields were shown to be dependent on the nature of interlayer anion in the hydrotalcite structure. The fragmentation and rearrangement reactions took place with moderate yield and selectivity, being of rather theoretical interest (*Scheme 119*).[122]



Scheme 119

III. OTHER SYNTHETIC APPROACHES BY MODIFIED CLAY CATALYSTS

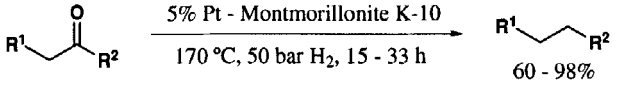
As illustrated in the previous chapters, clays are excellent catalysts in their own right, providing almost infinite application possibilities. However, as stable and durable inorganic materials, they can also serve as very useful support materials for the development of bifunc-

tional catalysts. The most frequent applications include, but are not limited to, the deposition of metals on clay surfaces, or immobilization of active metal complexes by ion-exchange. Both methods are widely used for the preparation stable, environmentally friendly bifunctional heterogeneous catalysts for organic synthesis. In this case, the processes will be grouped based on the type of reaction, which cannot be listed under acid or base catalysis. In these applications the clays act either as an acid catalyst or as an inert support.

1. Hydrogenation - Dehydrogenation

a) Chemoselective Hydrogenations

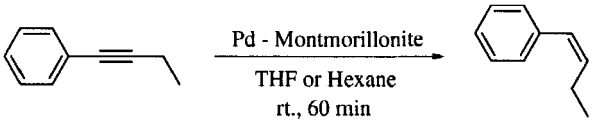
Compounds with a carbonyl group having an α-hydrogen atom were efficiently reduced to the corresponding alkane by catalytic reduction using 5% platinum on montmorillonite K-10 as an environmentally benign version of the Clemmensen reduction. The catalyst is easily prepared and highly stable (*Scheme 120*). The reaction occurred in a one-pot three-step sequence (hydrogenation to alcohol, dehydration to alkene, and hydrogenation to alkane).[123]



$R^1 = C_3H_7, C_4H_9, C_6H_{13}, (CH_3)_3C, C_6H_5$, etc.
$R^2 = CH_3, C_2H_5, C_3H_7$, etc.
$R^1, R^2 = -(CH_2)_3-, -(CH_2)_4-, 2\text{-}CH_3\text{-}(CH_2)_4-$, etc.

Scheme 120

Palladium incorporated in montmorillonite was used for the partial hydrogenation of 1-phenyl-1-butyne. Interestingly, catalysts containing higher amounts of palladium (0.46%) were less active, but more stereoselective (86 – 88%) toward the formation of *cis*-alkene, in contrast to montmorillonite containing less palladium (0.1%) (*Scheme 121*).[124]

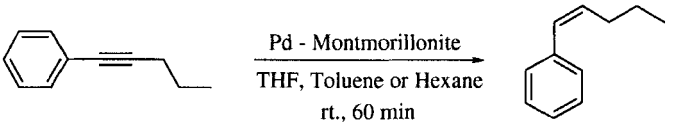


Pd (0.10%): Conv. 78%; Selectivity: 75%
Pd (0.46%): Conv. 40%; Selectivity: 88%

Scheme 121

1-Phenyl-1-pentyne was hydrogenated predominantly to the *cis*-alkene on montmorillonite-supported palladium, similar to the above mentioned catalysts, at room temperature in tetrahydrofuran, toluene or hexane. The catalytic activity and selectivity of the palladium montmorillonite was comparable to that of the Lindlar catalyst (*Scheme 122*).[125]

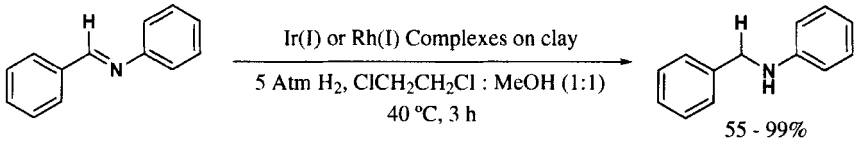
Iridium and rhodium-clay catalysts were prepared by immobilizing organometallic complexes on clays like montmorillonite K-10, sodium bentonite and lithium hectorite. The



Yield: 61%
Selectivity: 97%

Scheme 122

catalysts were used for the hydrogenation of *N*-benzylideneaniline. The catalytic activity of iridium (I) systems was superior (*Scheme 123*) to the other catalysts used in this study.[126]

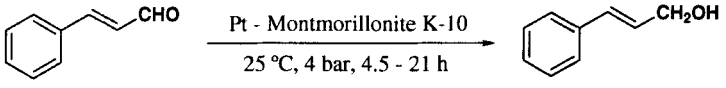


55 - 99%

Ir(I) Complexes: $[Ir(m\text{-}Cl)(COD)]_2$, $[Ir(COD)(PPh_3)_2]BF_3$, $[Ir(COD)(PPh_3)_2]PF_6$
Rh(I) Complex: $[Rh(COD)(PPh_3)_2]BF_4$

Scheme 123

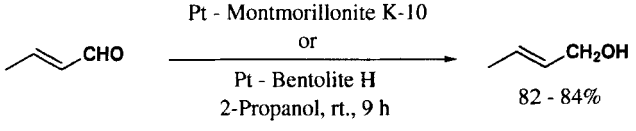
Chemoselective hydrogenation is an important and useful reaction for the synthesis of fine chemicals used in pharmaceuticals, perfumes, etc. 5% Platinum on montmorillonite K-10 catalyzed a highly selective hydrogenation of cinnamaldehyde to cinnamyl alcohol (*Scheme 124*).



Yield: approx. 90%
Selectivity: 99%

Scheme 124

Similar platinum-montmorillonite catalysts were more efficient and convenient for the catalytic hydrogenation of other unsaturated carbonyl compounds to the corresponding unsaturated alcohols. The process was described as bifunctional catalysis, when the acidic centers of the clay ensured the selective adsorption of the strongly nucleophilic carbonyl oxygen, making it an easier target for the hydrogenation.[127,128] This concept, namely montmorillonite K-10 and bentolite H supported with platinum, was applied for the hydrogenation of crotonaldehyde to generate the unsaturated alcohol. A self-poisoning of the metal over clay support was thought to inhibit the hydrogenation of the carbon – carbon double bond (*Scheme 125*).[129]

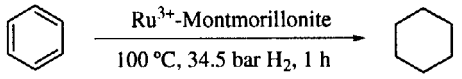


82 - 84%

Scheme 125

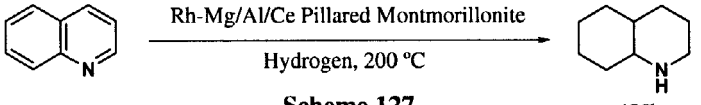
Benzene present in petroleum and diesel fuels is removed due to its carcinogenic activity. However, removal of benzene by solvent extraction methods decreases the octane

number of the gasoline. Thus reduction of benzene is an important process in the petroleum industry. Ru^{3+}- exchanged montmorillonite was used to hydrogenate benzene at 100 °C and 34.5 bars of hydrogen pressure. Additional Cu^{2+}-salts impregnated on montmorillonite increased the sulfur tolerance of Ru^{3+} ion-exchanged montmorillonite (*Scheme 126*).[130] The most likely explanation of the hydrogenation is that the Rh(III) and Cu(II)-ions are reduced to the corresponding metal (0) forms.



Scheme 126

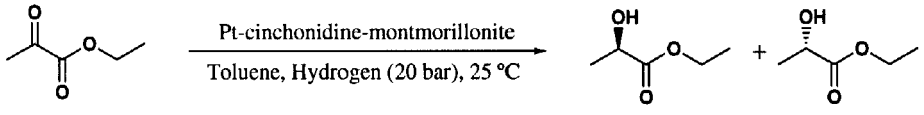
Rhodium (2 wt %) dispersed in Mg/Al/Ce pillared montmorillonite clay was prepared and used to hydrogenate quinoline to decahydroquinoline at 200 °C (*Scheme 127*).[131] The stereochemistry of the product decahydroquinoline was not discussed.



Scheme 127 42%

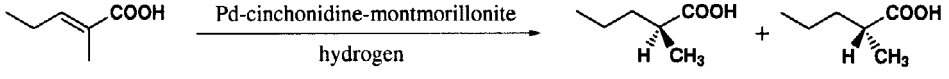
b) Enantioselective Hydrogenations

Platinum, palladium and rhodium supported on montmorillonite K-10 doped with cinchonidine as a chiral modifier were prepared and used for the enantioselective hydrogenation of ethyl pyruvate. The results suggest that the acidic support significantly contributed in the immobilization of the chiral modifier. Whereas both platinum and rhodium catalysts were found to be active, only platinum catalysts gave good enantioselectivities (up to 75% *ee* for *R*-isomer with 100% conversion) (*Scheme 128*).[132]



Scheme 128 (*R*)-Ethyl lactate (*S*)-Ethyl lactate

Platinum and palladium supported on montmorillonites containing immobilized cinchonidine were also prepared, characterized and used for the enantioselective hydrogenation of ethyl pyruvate and 2-methyl-2-pentenoic acid (*Scheme 129*).[133] Under optimized conditions



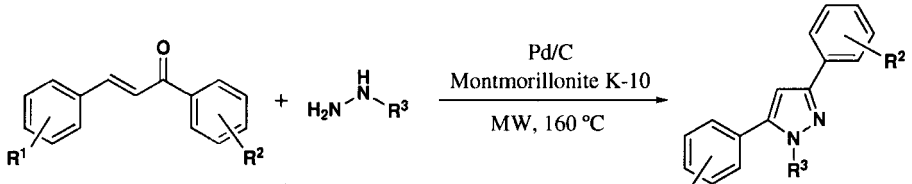
Scheme 129

platinum catalysts produced very high yields (up to 98%) and promising enantiomeric excesses (up to 56% ee) in ethyl pyruvate hydrogenation. The best Pt catalyst was also subjected to recycling studies. The authors reported no decline in either the activity or the enantioselectivity of the catalyst. Palladium catalysts, although gave excellent yields (up to 98%) only resulted in moderate enantioselectivities (~10% ee) in the hydrogenation of 2-methyl-2-pentenoic acid.

The cinchonidine-doped montmorillonite K-10-supported noble metal catalysts were extensively characterized and their thermal stabilities were determined.[134]

c) Dehydrogenations

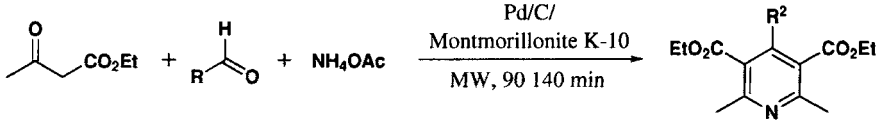
A novel one-pot synthesis of substituted pyrazoles from chalcones and hydrazines *via* a domino cyclization-dehydrogenation approach was carried out using a bifunctional noble metal-solid acid catalyst, Pd/C/montmorillonite K-10 and microwave irradiation under solvent-free conditions. The cyclization of chalcones with hydrazines readily took place on montmorillonite K-10 while the presence of Pd ensured the formation of the aromatic product through dehydrogenation. The reactions were complete in 30 minutes providing good to excellent yields (85-98%) with high selectivities (*Scheme 130*).[135]



R^1 = H, F,
R^2 = H, OCH_3, F, CH_3,
R^3 = CH_3, C_6H_5, 3-$CF_3C_6H_4$, 4-$NO_2C_6H_4$

Scheme 130

The same concept of bifunctional catalysis was applied in the microwave-assisted one-pot synthesis of substituted pyridines *via* a domino cyclization/oxidative aromatization approach from aldehydes, β-ketoesters and ammonium acetate. The method is an effective one-pot modification of the Hantzsch synthesis. The reaction takes place in relatively short reaction times under solvent-free conditions, and provides the products in good to excellent yields and with good selectivities (*Scheme 131*).[136]



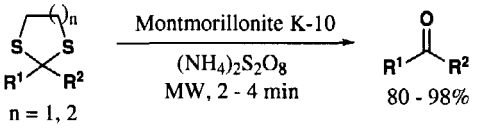
60 - 95%

R = C_6H_5, 4-BrC_6H_4, 4-ClC_6H_4, 4-FC_6H_4, 4-$NO_2C_6H_4$, 4-$CH_3C_6H_4$, 4-CNC_6H_4, C_7H_{15}, $(CH_3)_2CHCH_2$, 2-Naphthyl, $C_6H_5CH(CH_3)$, $C_6H_5CH_2CH_2$, etc.

Scheme 131

4. Oxidation

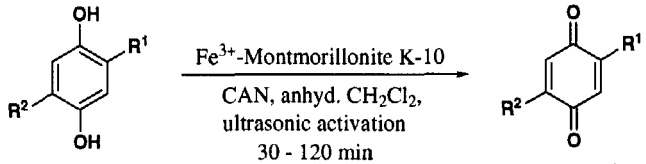
1,3-Dithianes and 1,3-dithiolanes underwent smooth oxidative deprotection to the corresponding aldehydes or ketones in the presence of ammonium persulfate on wet montmorillonite K-10 support under microwave irradiation (*Scheme 132*).[137]



R^1 = C_6H_4, 2-HOC_6H_4, 2-$CH_3OC_6H_4$, 2-$AcOC_6H_4$, C_2H_4, $(CH_3)_3C$, $C_6H_5CH{=}CH$, etc.
R^2 = H, CH_3, C_6H_5, $H_2NC_6H_4$
R^1, R^2 = cyclohexyl

Scheme 132

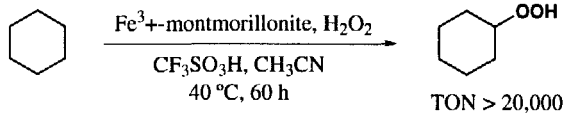
Hydroquinones were quantitatively oxidized to quinones by Fe^{3+}- exchanged montmorillonite K-10 doped with cerium (IV) ammonium nitrate (CAN) using ultrasonic activation (*Scheme 133*).[138]



R^1 = H, CH_3, $C_3H_7C(CH_3)_2$, Cl, Br, CH_3O
R^2 = H, Cl

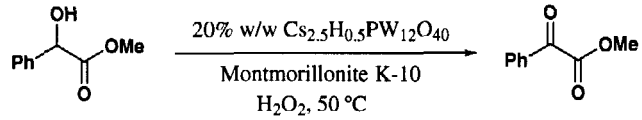
Scheme 133

The oxidation of cyclohexane with hydrogen peroxide was carried out with a chain-like Fe^{3+}-species, which contained Fe-O-Fe units within the interlayer space of the montmorillonite. The reaction produced cyclohexyl hydroperoxides with very high turnover numbers (TON 21,000 after 60 h) (*Scheme 134*); however, isolated yields were not given.[139]



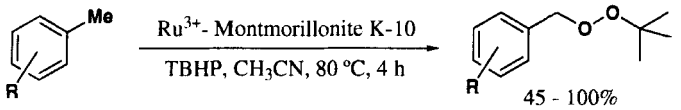
Scheme 134

Methyl phenylglyoxylate was prepared by oxidation of methyl mandelate using hydrogen peroxide in the presence of cesium salt of dodecatungstophosphoric acid (20% w/w) supported on montmorillonite K-10. The catalyst appears to be reusable (*Scheme 135*).[140]



Scheme 135

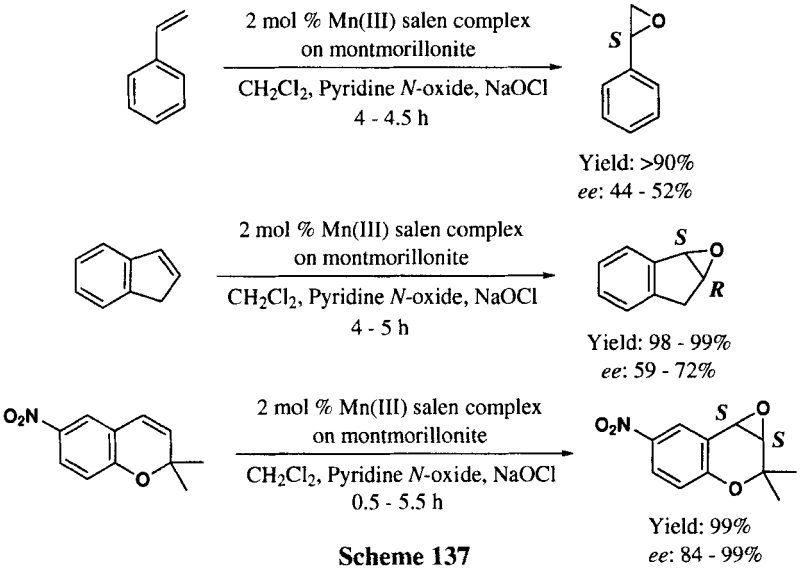
Alkyl arenes were converted to the corresponding *tert*-butyl benzyl peroxides by benzylic oxidation in the presence of catalytic amount of Ru^{3+}-exchanged montmorillonite K-10 and 70% aq. *tert*-butyl hydroperoxide (TBHP) as oxidant at 80 °C (*Scheme 136*).[141]



R = H, 2-CH_3, 4-CH_3, 4-CH_3COO, 3,5-$(CH_3)_2$
and
Ethyl benzene, 4-Cymene, Tetralin, Tetrahydrofuran,
3,4-Dihydropyran, Isobutylbenzene, Flourene

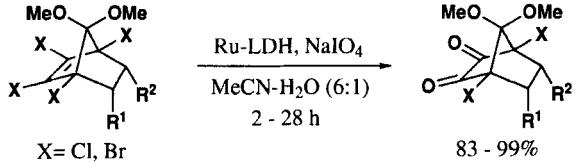
Scheme 136

A Mn(III)-salen complex immobilized on montmorillonite in the presence of pyridine *N*-oxide and sodium perchlorate was used for the enantioselective epoxidation of styrene, indene and 2,2-dimethyl-6-nitrochromene in high yields (*Scheme 137*).[142] The enantiomeric excess appeared to be strongly dependent on the structure of the substrate.



Scheme 137

1,2-Dihaloalkene moities present in tetrahalonorbornyl derivatives were oxidized to the corresponding α-diketones by layered double hydroxide (LDH) supported ruthenium (III) catalyst (*Scheme 138*).[143]



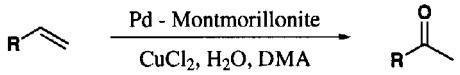
X= Cl, Br

83 - 99%

R^1 = H; R^2 = C_6H_5, CH_2Cl, CO_2Me
R^1, R^2 = -$(CH_2)_4$-, -CH_2OCH_2-

Scheme 138

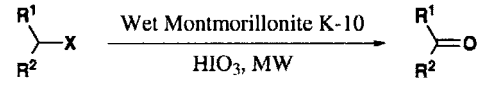
Palladium ion-exchanged montmorillonite in the presence of $CuCl_2$, was developed as a highly efficient heterogeneous catalyst for the Wacker oxidation of terminal olefins to the corresponding methyl ketones. The catalyst was reusable and retained its activity and selectivity (*Scheme 139*).[144]



R = C_4H_9, C_6H_{13}, $C_{10}H_{21}$, $C_{14}H_{29}$, $C_{18}H_{37}$, $CH_3O_2C(CH_2)_8$, NCC_3H_6, $HO(CH_2)_8$, cyclohexyl, etc.

Scheme 139

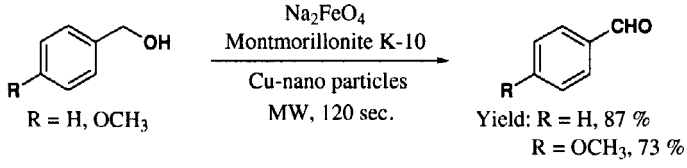
Benzyl halides and alkyl halides were oxidized to the corresponding aldehydes and ketones by wet montmorillonite K-10 in the presence of periodic acid as oxidizing agent under microwave irradiation. The clay was reusable after activation (*Scheme 140*).[145]



R^1 = C_6H_5, 4-BrC_6H_4, 4-ClC_6H_4, 4-$O_2NC_6H_4$, 4-$CH_3C_6H_4$, 3-$O_2NC_6H_4$, 4-FC_6H_4, a-$C_{10}H_7$
R^2 = H, C_6H_5, 4-ClC_6H_4

Scheme 140

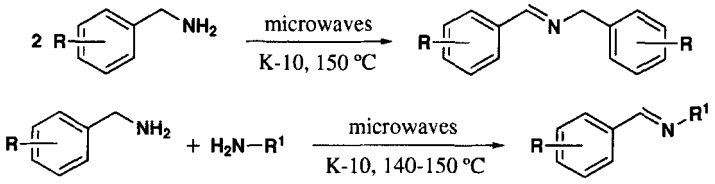
Sodium ferrate in the presence of copper nano particles adsorbed on montmorillonite K-10 were used under microwave irradiation for the oxidation of benzyl alcohol, 4-methoxy benzyl alcohol, benzaldehyde and 4-nitrobenzaldehyde (*Scheme 141*). However, polymerization was observed for aniline, 4-methylaniline and phenols (phenol, catechol, resorcinol, 4-methylphenol).[146]



Scheme 141

A montmorillonite K-10 catalyzed microwave-assisted oxidative coupling of amines resulting in a wide spectrum of aldimines. Substituted benzylamines readily underwent self-coupling reactions to produce benzylidene benzylamines in 85-98% yield, while aliphatic amines and anilines did not form self-coupled products. A mixture of a benzylamine and an aniline or

aliphatic amine respectively, effectively and selectively produces mixed imines, such as benzylidene anilines (up to 95% yield), and benzylidene alkylamines (up to 50% yield) (*Scheme 142*).[147]

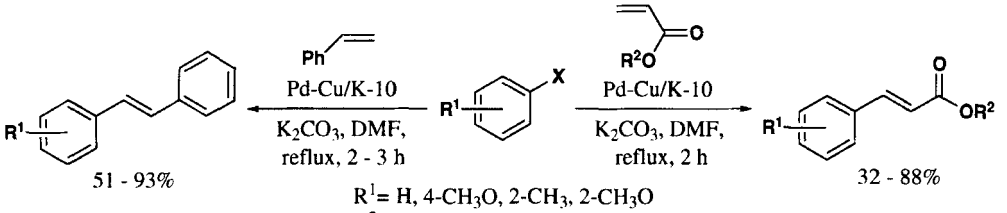


R^1 = substituted Ph, alkyl

Scheme 142

5. Heck Reaction

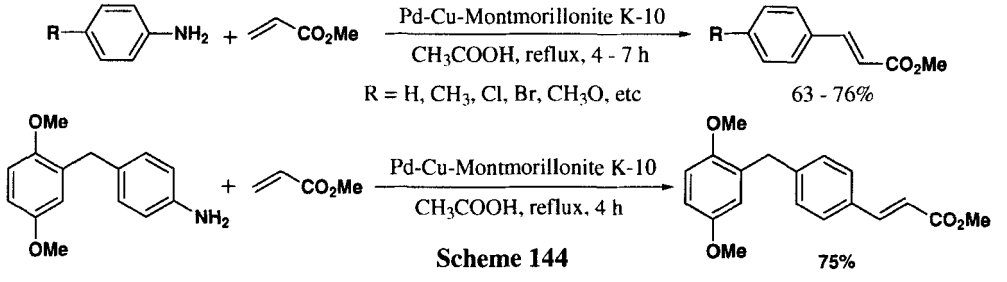
The Heck vinylation reaction between aryl halides and acrylates or styrenes to form alkyl (*E*)-cinnamates or (*E*)-stilbenes was efficiently catalyzed by palladium and copper ion-exchanged montmorillonite K-10 in the presence of potassium carbonate in dimethylformamide under reflux conditions (*Scheme 143*).[148]



R^1= H, 4-CH_3O, 2-CH_3, 2-CH_3O
R^2= CH_3, C_2H_5
X= I, Br

Scheme 143

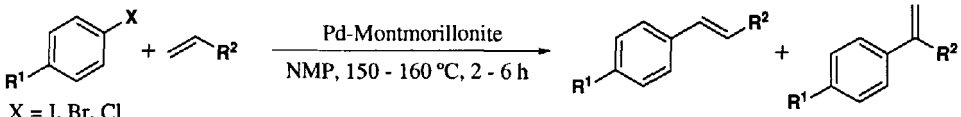
Palladium (II)-chloride and copper (II)-nitrate intercalated montmorillonite K-10 clay was used as a catalyst for Heck vinylation reaction of different substituted anilines with vinyl acetate to give substituted methyl cinnamates in high yields (*Scheme 144*).[149]



Scheme 144

Two new palladium-montmorillonite catalysts were recently prepared and their catalytic activity in intermolecular Heck reaction was studied (*Scheme 145*). Both catalysts exhibited high activity towards the Heck coupling reaction of aromatic bromides and activated

aromatic chlorides. The catalysts were easy to prepare, insensitive to air and moisture, showed high turnover numbers and could be recycled, though a decrease in activity was noted.[150]



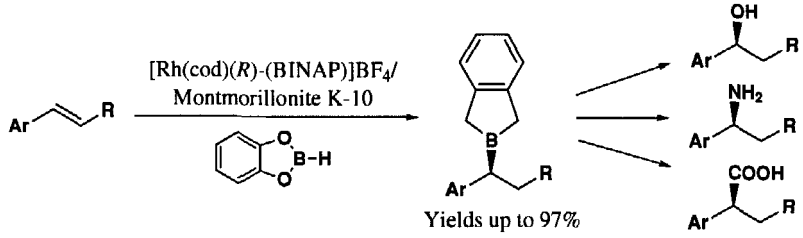
X = I, Br, Cl
R^1 = H, Cl, OCH_3, $COCH_3$
R^2 = C_6H_5, CO_2CH_3

Conv. 73 - 100 %
Yield 68 - 99 %

Scheme 145

6. Hydroboration

A new class of clay catalysts was developed by the immobilization of [Rh(COD)(*R*)-(BINAP)]BF_4 complex on montmorillonites for the hydroboration of vinyl arenes. Using catelcholborane, the reaction proceeded with excellent yields (97%) and *ee* values (89%) (*Scheme 146*). Comparative investigations showed that the immobilized catalyst gave slightly lower yields, but higher enantioselectivities than the homogeneous application. Repeated reactions using the same catalyst without reactivation showed similar yields and *ee*-s.[151]



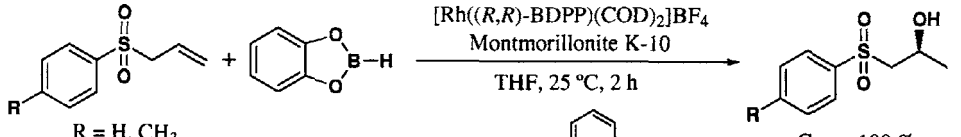
Yields up to 97%
ee up to 89%

Ar = C_6H_5, 4-FC_6H_4, 4-$CH_3C_6H_4$, 2-Naphthyl
R = H, CH_3 (only when Ar = C_6H_5)

Scheme 146

The approach has recently been expanded with the use of several other chiral rhodium complexes [ligands: (*R*)-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl, (*S,S*)-2,4-*bis*(diphenylphosphino) pentane, (*S*)-2-diphenylphosphino-1-(1'-isoquinolyl)naphthalene] and a wide variety of vinylarenes.[152]

Hydroboration of heterofunctional allylic systems were carried out using catecholborane in neutral or cationic rhodium complexes, immobilized on clay, modified with P-P and P-N bidentate chiral ligands (*Scheme 147*). The catalyst could be recycled.[153]



R = H, CH_3

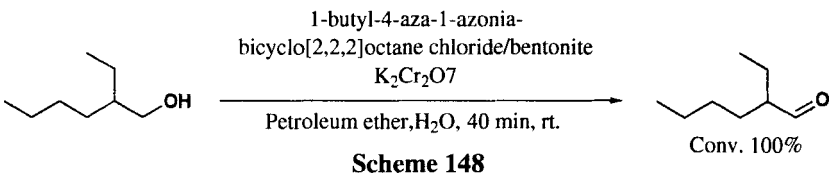
BDPP =

Conv. 100 %
ee 30 - 32 %

Scheme 147

7. Phase Transfer Catalysis

Bentonite clay modified by the surfactant 1-butyl-4-aza-1-azonia bicyclo[2.2.2]octane chloride acted as an efficient phase-transfer catalyst for the oxidation of the lipophilic alcohol 2-ethyl-1-hexanol by potassium dichromate (*Scheme 148*).[154]



Scheme 148

V. CONCLUSIONS AND OUTLOOK

Over the past three decades, clay catalysts became a mainstream solid acid of choice for organic synthesis. The progress made in this area prompted suppliers to develop industrial synthesis for the most successful catalysts. Today many of these materials are readily available providing a boost for their synthetic applications. The inexpensive and environmentally friendly nature of these solid acids led to their wide use in research laboratories. Due to their structural features, they can easily be modified with different metal cations, or organic/organometallic compounds resulting in new catalysts of potential importance. Both the modified and natural clays can be applied to catalyze a broad variety of chemical transformations, thus providing exceptional importance for these materials in the development of new synthetic processes. The recent trends of strengthening environmental regulations and safety concerns generate even further interest in these catalysts. As their acidity is higher than that of zeolites, and their mechanical properties (durability, surface area etc.) are much better than that of acidic ion-exchange resins, they are considered as the environmentally benign acid catalysts of the future.

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