CHAPTER II

Montmorillonite K-10 Catalyzed Friedel-Crafts Benzylation and Allylation with Activated Esters

\[
\begin{align*}
\text{R} \cdot \text{C}_6\text{H}_5 + \text{Ph} \cdot \text{C}_2\text{H}_4 \cdot \text{O} \cdot \text{Ph} & \xrightarrow{\text{Montmorillonite K-10}} \text{R} \cdot \text{C}_6\text{H}_5 \cdot \text{Ph} \\
\text{R} \cdot \text{C}_6\text{H}_5 + \text{Ph} \cdot \text{C}_2\text{H}_4 \cdot \text{O} & \xrightarrow{\text{Montmorillonite K-10}} \text{R} \cdot \text{C}_6\text{H}_5 \cdot \text{C}_2\text{H}_4 \cdot \text{Ph}
\end{align*}
\]
dioxane, reflux
CHAPTER II

Points to be Studied:

1. Introduction to Friedel-Crafts Reactions
2. Catalyst in Friedel-Crafts Reaction
3. Various Alkylating Agents
4. Literature Survey for Friedel-Crafts Benzylation and Allylation Reaction
5. Clay Catalyzed Friedel-Crafts Alkylation and Allylation Reaction
6. Present Work: Montmorillonite K-10 Catalyzed Friedel-Crafts Benzylation and Allylation with Activated Esters.
7. Results and Discussion
8. Reaction Mechanism
9. Experimental Section
10. Characterization of the Products
11. Merits of the Methodology and conclusion.
12. References
1] Introduction to Friedel-Crafts Reaction

Friedel-Crafts acylation and alkylation are among the most fundamental and useful reactions for introducing carbon substituents to aromatic rings.\(^1\) In particular, the alkylation of an aromatic ring through the Friedel-Crafts reaction is of great synthetic significance in view of laboratory synthesis and industrial production. For example, alkylbenzenes with 10-14 side chain carbon atoms are starting material for the manufacture of sulfonates which are important raw materials for the industrial production of anion-active detergents and polymers.\(^2\)

As a consequence, the annual production of alkylbenzenes for this purpose is estimated to be over one million tons in Western Europe, USA and Japan. The other industrial processes for high octane gasoline, ethyl benzene, synthetic rubber and plastics are also based indirectly on the fundamental Friedel-Crafts alkylation reaction.\(^3\)

The antioxidant and antibacterial activity of alkyl phenols also demonstrate the practical significance of Friedel-Crafts reactions.\(^4\)

Friedel-Crafts alkylation of the aromatic nucleus has been traditionally carried out by using Lewis acids and the corresponding alkyl halides.\(^5\)

\[ \text{Aromatic Ring} + R^1 - X \xrightarrow{\text{Lewis acid}} \text{Alkylated Aromatic Ring} \]

In the course of more than 100 years of Friedel-Crafts chemistry, a number of variations and extensions in the use of acid catalyst and alkylation reagents has been observed.\(^6\) There is an unending list for a variety of catalyst under homogenous as well as heterogeneous conditions for a typical Friedel-Crafts alkylation reaction.
2] Catalyst in Friedel-Crafts Reactions:

The Friedel-Crafts reaction is a typical aromatic electrophilic substitution reaction. The electrophile is a carbocation generated from the reaction of alkylating agent with the acid catalyst. Regardless of which alkylating reagent is used, a catalyst is nearly always required. The catalyst employed for this reaction is usually acidic in nature, Lewis or Bronsted acid. Depending on the nature of catalyst, homogeneous as well as heterogeneous catalytic conditions can also prevail for Friedel-Crafts reactions. Following are the few catalysts which are commonly reported for Friedel-Crafts alkylation reactions.

A] Lewis Acids:

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlCl₃</td>
<td>SbCl₅</td>
</tr>
<tr>
<td>BF₃OEt₂</td>
<td>TiCl₄</td>
</tr>
<tr>
<td>FeCl₃</td>
<td>ZrCl₄</td>
</tr>
<tr>
<td>SnCl₄</td>
<td>GaCl₃</td>
</tr>
<tr>
<td>ZnCl₂</td>
<td>ScCl₃</td>
</tr>
<tr>
<td>Hf(OTf)₄</td>
<td>InCl₃</td>
</tr>
<tr>
<td></td>
<td>Cl₂Si(OTf)₂</td>
</tr>
</tbody>
</table>

RE(OTf)₃ where RE is rare earth
Elements like Sc, Yb, Nd, Sm, Y, etc.

B] Bronsted Acids:

<table>
<thead>
<tr>
<th>Acid</th>
<th>Acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂SO₄</td>
<td>CF₃SO₃H</td>
</tr>
<tr>
<td>HF</td>
<td>CH₃SO₃H</td>
</tr>
<tr>
<td>(H₃PO₄)ₙ</td>
<td>C₆H₅SO₃H</td>
</tr>
<tr>
<td></td>
<td>p-TsOH</td>
</tr>
</tbody>
</table>

C] Solid Acids:

Nafion –H
Montmorillonite K-10
FeCl₃, ZnCl₂, AlCl₃ impregnated on Montmorillonite K-10
Bentonite
Amberlyte-15
Zeolite
General features of the catalysts in Friedel-Crafts reactions:

The important silent features of the most commonly used acid catalyst are discussed below:

1] **Aluminium Trichloride (AlCl₃)**

Anhydrous AlCl₃ as a Lewis acid was introduced by Friedel and Crafts in their alkylation and acylation reaction of aromatics. It has gained wide recognition, despite some unfavorable properties such as:

- limited solubility in organic solvents.
- sublimation at higher temperature.

2] **Boron Trifluoride (BF₃·OEt₂)**

Boron trifluoride has also become a widely used catalyst since 1920s.

- BF₃ is a low boiling gas (bp -101 °C).
- It is used in the form of convenient complexes such as ether complexes despite their low reactivity.

The common drawbacks of widely used AlCl₃ and BF₃ are listed below:

- More than stoichiometric quantity is required, particularly in acylation reaction because of their tendency to coordinate with the produced aromatic ketones.
- In some cases AlCl₃ is known to result in extensive undesirable side reactions such as degradation, polymerization and isomerization.
- The conditions employing AlCl₃ and BF₃ co-produces hydrogen halide which often induces side reactions.
- A large amount of AlCl₃ and its waste after aqueous work-up procedures often cause serious environmental problems.
- Both of them can not be reused after aqueous work-up.

3] Rare Earth Metal Triflates, RE(OTf)₃:

In recent years, there is a growing interest in the use of rare earth metal triflates⁸ as Lewis acids in Friedel-Crafts acylation and alkylation because of the following facts:

- RE(OTf)₃ could be easily recovered after the reactions were completed and could be reused without loss of activity.
- RE(OTf)₃ are resistant to aqueous media. So the reaction can also be performed in an undried solvent without any special care.
- Reaction employing RE(OTf)₃ does not produce hydrogen halides as the byproduct, thereby minimizing the side reactions.
- Catalytic quantity is sufficient to get the quantitative yields of Friedel-Crafts reactions.

The common rare earth metals such as Sc, Y, La, Pr, Nd, Sm and Eu are used as triflates for the Friedel-Crafts reaction.

Sc(OTf)₃ is the most active catalyst among RE(OTf)₃. It can also catalyze the reductive Friedel-Crafts reactions.⁹

In summary, RE(OTf)₃ is an ideal and promising catalyst to solve troublesome environmental problems caused by the Lewis acid-promoted reactions used for industrial processes.
4] H₂SO₄ and HF:

Protic acids such as anhydrous HF and concentrated H₂SO₄ have also been successfully used in the alkylation of the aromatic nucleus using simple olefins and alcohols.¹⁰

These acids are notoriously corrosive, highly toxic and hazardous.

5] Organic Sulfonic Acids:

Various organic sulphonic acids such as perfluorosulfonic acid,¹¹ methanesulfonic acid¹² and benzenesulfonic acid¹³ have been occasionally used to catalyze Friedel-Crafts alkylations.

p- Toluene sulfonic Acid Monohydrate (TsOH)¹⁴

TsOH is an efficient and excellent catalyst for the Friedel-Crafts reaction of aromatic nucleus with activated alkyl halides, alkenes, or tosylates under mild conditions in an open atmosphere.¹⁵ The important advantages of TsOH as the catalyst for Friedel-Crafts reactions are:

- Low cost of the catalyst.
- Minimum generation of environmentally unfriendly waste.
- Most of the catalyst can be recovered by simple filtration and reused.
3] Various Alkylating Agents in Friedel-Crafts Alkylation Reaction

A variety of alkylating agents for effecting the Friedel-Crafts alkylation of aromatic nucleus has been successfully employed.


These alkylating agents react with a suitable acid catalyst to generate a carbocation, which in turn, attacks an aromatic nucleus to afford the alkylated product.

\[
\text{Alkylating agent + Acid} \xrightarrow{\text{Acid}} \text{Carbocation, a potential electrophile} \xrightarrow{\text{Attack}} \text{Alkylated Product}
\]

General Features of Various Alkylating Agents

3.1] Alkyl Halides:

Alkyl halides have been employed as one of the suitable electrophiles for the synthesis of various aromatic compounds due to their appropriate stability and reactivity. Very often, the mildest conditions are associated with the procedure of the reaction. However, the lacrimatic nature of most of the alkyl halide is an unpleasant feature of the procedure. The hydrogen halide formed as a side product can promote side reactions.
3.2] Alcohols:

Alcohols have been commonly used as an alkylating agent. Benzyl alcohol and allyl alcohol are frequently used in several Friedel-Crafts reaction.\textsuperscript{16-17}

- The reaction employing alcohols usually requires high temperature even if it is accelerated by acid catalysts such as TeCl\(_4\),\textsuperscript{16} Nafion-H\textsuperscript{17} and Sc(OTf)\(_3\).\textsuperscript{9b}

- It is necessary to use an excess amount of ordinary Lewis acids to produce the alkylated compounds in high yields since free hydroxyl groups in alcohol sometimes deactivate the catalysts.

- Friedel-Crafts reactions with alcohols as the alkylating agents are usually carried out under strictly anhydrous conditions. The presence of a small amount of water lowers the yield drastically, because the catalyst is rapidly decomposed or deactivated by the moisture.

- Sometimes isomerized alkylation product is formed with the use of allylic type alcohol such as crotyl alcohol and cinnamyl alcohol.

- Bronated acids, especially H\(_2\)SO\(_4\) are often used to catalyze alkylation with alcohols.

3.3] Olefins:

Olefins are especially good alkylating agents.\textsuperscript{15}

- The self cationic polymerization of olefins is a potentially important side reactions. So procedure sometimes demand more than stoichiometric quantity of olefins.
In recent years, a number of studies on aromatic substitution using olefins by the action of organometallic reagents, especially palladium and copper containing, have been reported.

3.4] Ethers:

There have not been many trials for the development of the Friedel-Crafts alkylation reaction using ordinary ethers. However, allyl or benzyl silyl ethers can act as a source of electrophile in presence of a suitable Lewis acid.\(^\text{18}\) For example,

\[
\begin{align*}
\text{Ph} & \quad \text{Hf(OTf)}_4 (0.1 \text{ eq.}) \\
\ \text{50 °C, 4.5 h} & \quad 58 \%
\end{align*}
\]

In the above reaction,

- Only catalytic quantity of the Lewis acid is employed.
- No deactivation of the catalyst is observed.
- Mild reaction conditions compared to alcohol as alkylating agents.

3.5] Carbonyl Compounds:

When carboxylic esters are the reagents, there is a competition between alkylation and acylation. Though this competition can often be controlled by choice of catalyst, and alkylation is usually favoured, carboxylic esters are not often employed in Friedel-Crafts reactions.

Reductive Friedel-Crafts alkylation of aromatics with ketones and aldehydes is a novel synthetic tool. Recently, a combination of Lewis acid, \(\text{InCl}_3\) and a hydride donor, \(\text{Me}_2\text{SiClH}\) has been successfully used in the reductive Friedel-Crafts alkylation of aromatics.\(^\text{19}\)
Me₂SiClH + R¹R² + ArH (excess) → InCl₃ (5 mol %) → R¹R²Ar

In this reaction the conditions employed are very mild, and even low reactive aromatics such as bromobenzene can be effectively alkylated. In addition, only 5 mol % of InCl₃ is sufficient.

In another report, a catalytic quantity of Sc(OTf)₃ can induce an unprecedented reductive Friedel-Crafts benzylation of an aromatic compound using arenecarbaldehyde.²⁰

- Catalytic quantity of Sc(OTf)₃ is recoverable and reusable after the synthetic reaction.

- 1,3-Propanediol acts as the hydride source. In its absence, reaction does not proceed.
4] Literature Survey for Friedel-Crafts Benzylation and Allylation Reaction:

Benzylation and allylation of the aromatic nucleus has been carried out in a variety of ways.

4.1] Solid Superacid – Catalyzed Benzylation with Benzyl Alcohol:

Nofion-H, a super-acidic perfluorinated resinsulfonic acid, is a very good catalyst for a gas phase alkylations with alkyl halides, alcohols, or olefins.\textsuperscript{21}

Olah et. al. have reported the Friedel-Crafts benzylation of aromatics with benzyl alcohol in presence of the catalyst Nation-H. For example,

\[
\begin{align*}
\text{C}_{6}\text{H}_{5}\text{OH} & + \text{C}_{6}\text{H}_{5} & \xrightarrow{\text{Nafion-H (10 wt%)}} & \text{C}_{6}\text{H}_{5}\text{C}_{6}\text{H}_{5} \\
\text{97}\% & & & \\
\end{align*}
\]

- It is an example of heterogeneous Friedel-Crafts reaction.
- Only catalytic quantity (10 wt %) of Nafion-H is necessary.
- Catalyst can be recovered and reused.
- Water is the only byproduct of the reaction. It does not deactivate the catalyst.
- In some cases, a competitive ether formation takes place. For examples.

\[
\begin{align*}
\text{C}_{6}\text{H}_{5}\text{OH} & \xrightarrow{\text{Nafion-H}} \text{C}_{6}\text{H}_{5} + \text{C}_{6}\text{H}_{5}\text{O} & \xrightarrow{\text{Benzene 90-95 °C}} & \text{C}_{6}\text{H}_{5}\text{C}_{6}\text{H}_{5} \text{C}_{6}\text{H}_{5} \\
\text{69}\% & + & \text{22}\% & \\
\end{align*}
\]

- Reaction stops with monobenzylation product formation.
4.2] Benzylation and Allylation of Aromatics with Benzyl or Allyl Silyl Ethers\textsuperscript{18} using $\text{Cl}_2\text{Si(OTf)}_2$ or $\text{Hf(OTf)}_4$:

- The first time use of benzyl or allyl silyl ethers as alkylating agents is an attractive feature of the methodology.

- Catalytic quantity of $\text{Hf(OTf)}_4$ is sufficient which is not normally the case with free benzyl on allyl alcohol as an alkylating agent.

- Mild reaction conditions (under 50 °C).

\[
\begin{align*}
\text{R}_1\text{R}_2\text{C} &\text{OSiMe}_3 \xrightarrow{\text{Hf(OTf)}_4, (0.1 \text{ eq.})} \text{R}_1\text{R}_2\text{C} &\text{OSiMe}_3 \\
\text{toluene, 50 °C, 4.5h} &\rightarrow \text{R}_1\text{R}_2\text{C} &\text{CH}_3 \\
\end{align*}
\]

\[
\begin{align*}
\text{Ph} &\text{OSiMe}_3 + \text{R}_1\text{R}_2\text{C} \xrightarrow{\text{Cl}_2\text{Si(OTf)}_2 \text{ or } \text{Hf(OTf)}_4, (0.1 \text{ eq.})} \text{R}_1\text{R}_2\text{C} \text{Ph} \\
\text{solvent} &\rightarrow \text{R}_1\text{R}_2\text{C} \text{Ph} \\
50 °C, 4.5h &
\end{align*}
\]

4.3] Scandium(III)Triflate-Catalyzed Benzylation and Allylation with Benzyl Alcohol and Allylic Alcohol:

The $\text{Sc(OTf)}_3$-catalyzed Friedel-Crafts alkylation reaction with benzyl alcohol and allyl alcohol as the alkylating agents affords a diarylmethane or an allylbenzene derivative in good to excellent yields.\textsuperscript{22}

\[
\begin{align*}
\text{PhOH} + \text{R}_2\text{C} \xrightarrow{\text{cat. Sc(OTf)}_3} \text{R}_1\text{R}_2\text{C} \\
\text{R}_2\text{C} &\text{OH} \xrightarrow{\text{Sc(OTf)}_3 (10 \text{ md\%})} \text{R}_3\text{R}_4\text{C} \\
\end{align*}
\]
- Catalytic quantity of Sc(OTf)_3 is sufficient.

- The reaction can be performed in an undried solvent without any special care.

- The catalyst can be recycled.

- The use of Sc(OTf)_3 is logically extended to the novel reductive Friedel-Crafts benzylation of aromatics with benzaldehyde in presence of 1,3-propanediol as a hydride source.

\[
\text{cat. Sc(OTf)}_3 (10 \text{ mol%}) \]

4.4] Allylation of Aromatic Compounds with Allyltrimethylsilane Using a Combination of Iodosylbenzene and BF_3.OEt_2

The reaction of allyltrimethylsilane with the electron rich aromatics using hypervalent iodine reagent, iodosylbenzene and BF_3.OEt_2 leads to an efficient allylation product.²³

- The first time use of allyltrimethylsilane is an attractive feature of the methodology.

- No polyallylation product formation.

- Success of the reaction is due to hypervalent iodine reagent, iodosylbenzene.

- A trace amount of o-allyliodobenzene as a side product was detected in all the reactions of aromatics.
4.5] Allylation of the Aromatic Compounds with Allylic Chlorides Catalyzed by Indium Metal

The allylation reaction of the aromatic compounds with allylic chlorides using a catalytic amount of indium in the presence CaCO₃/4 Å molecular sieves has been reported.²⁴

- The use of a solid base, CaCO₃ in combination with 4Å molecular sieves promotes the scavenging of liberated hydrogen chloride. This inhibits the side reactions.

- Allylation product is formed with the isomerization of a double bond.

- Mild reaction conditions.

- Indium metal is reusable after the reaction work up without loss of activity.
4.6] Reductive Friedel-Crafts Benzylation of Aromatics Catalyzed by InCl₃:

Reductive Friedel-Crafts alkylation of aromatics with ketones or aldehydes was catalyzed by a novel Lewis acid catalyst, InCl₃ in combination with hydrosilane as a hydride source and as a co-catalyst.¹⁹

\[
\text{Me}_2\text{SiCl}_2 + \overset{\text{O}}{\overset{\text{FG}}{\overset{\text{Ar}}{\overset{\text{excess}}{\text{R¹ R²}}}}} \quad \overset{\text{InCl₃ (5 mol %)}}{\rightarrow} \quad \overset{\text{R¹ R²}}{\overset{\text{Ar}}{\text{FG}}}
\]

- Reductive Friedel-Crafts alkylation with ketones and aldehydes is a huge and novel functional group manipulation.
- Chemoselective utilization of ketone moieties as alkylating reagents took place even in the presence of halogen, ester, or ether moieties which are very susceptible under traditional Friedel-Crafts conditions.

\[
\text{Me}_2\text{SiCl}_2 + \overset{\text{O}}{\overset{\text{FG}}{\overset{\text{Ph}}{\overset{\text{excess}}{\text{Ar}}}}} \quad \overset{\text{InCl₃ (5 mol %)}}{\rightarrow} \quad \overset{\text{Ph}}{\overset{\text{FG}}{\overset{\text{Ar}}{\text{FG}}}}
\]

FG may be halogen, ester or ether

- The studied reaction mechanism of this methodology provides the following various means for carrying out the benzylation reaction.

\[
\text{PhCHO} + \overset{\text{HSiMe}_2\text{Cl}}{\overset{\text{InCl₃ (5 mol %)}}{\text{Benzene}}} \rightarrow \left[ \text{PhCH}_{2}\text{Cl} \right] \rightarrow \text{PhCH}_{2}\text{Ph} \quad 79 \%
\]

1.0 mmol 1.2 mmol 25 °C, 14h
Any of the above reaction does not proceed at all in absence of silicon catalyst such as Me₂SiHCl, Me₃SiCl and Me₃SiOTf.

4.7] Copper Promoted Allylation of Phenols

Phenols can be allylated at an ortho-position by use of a mixture of anhydrous copper(II) perchlorate and copper metal powder. In this case, allyl chloride is an allylating agent.

- Regioselective O-allylation.
- Almost neutral conditions of the reaction.
- Reaction is restricted only to phenolic aromatics.
- Isomerization of the double bond occurs in the allylated product.
Clay catalysts are increasingly being used as heterogeneous catalysts for Friedel-Crafts alkylation reaction due to their chemo and regioselectivity, good efficiency and mild reaction conditions. The commercially available Montmorillonite K-10 has been extensively used in several Friedel-Crafts alkylation reactions. It has both Bronsted and Lewis acid sites. In addition to this, they are cheap, can be recycled and are ecofriendly compared to homogeneous acid catalysts. A pioneer in clay catalysis named P. Laszlo has described the clays as the most outstanding catalysts for Friedel-Crafts reactions due to:

- high yields
- high conversions
- reduced reaction times
- absence of polyalkylation
- lack of rearrangement
- reduction of amount of catalyst necessary
- elimination of toxic wastes (aluminium derivatives).

In the following literature survey, we have emphasized more on the recent use of Montmorillonite K-10 for Friedel-Crafts reactions.
5.1] Synthesis of Phenolic Sesquiterpene:

The synthesis of phenolic sesquiterpene such as curcuphenol and sesquiterpene have been achieved with the Montmorillonite K-10 catalyzed Friedel-Crafts reaction of substituted phenols.

- Reactions are carried out in ‘dry media’ i.e. with substrate as a solvent.

- Montmorillonite K-10 catalyzed Friedel-Crafts reaction is a key step in the overall synthesis of phenolic sesquiterpene.

- In the latter reaction Montmorillonite K-10 plays a dual role in promoting Friedel-Crafts reaction as well as in deprotection of ketal.
5.2] Synthesis of 1-Arylalkanes:

The production of biodegradable 1-arylalkanes is of significance for the detergents and lubricant industries. This 1-arylalkane can be produced by the following two step sequence.²⁸

\[
\begin{align*}
\text{CsH}_n\text{CH}=\text{CHCH}_2\text{OH} & \quad \xrightarrow{\text{Mont. K-10}} \quad \text{C}_5\text{H}_9\text{CH(OH)CH}=\text{CH}_2 \\
& \quad \xrightarrow{\text{H}_2} \quad \text{Pd / C Cat.} \quad 79 - 89\% \\
\end{align*}
\]

- Again Montmorillonite K-10 catalyzed Friedel-Crafts allylation is a key step in the synthesis of such a valuable 1-arylalkanes.

- The report also described other solid acids such as Amberlite-15, silica and zeolites for the key Friedel-Crafts allylation with allyl alcohol. But Montmorillonite K-10 was found to be the most efficient of all.

5.3] Friedel-Crafts Allylation with primary, secondary and tertiary alcohols²⁹:

Monoalkylation of benzene with primary, secondary, tertiary alcohols took place in high yields when Montmorillonite K-10 was used as acid catalyst. The methodology is particularly focused on the long chain alkylarene synthesis by using a variety of alcohols such as octane-1-ol, hexadecan-1-ol, hexadecan-2-ol, 2-methylpentadecan-2-ol and 2-methylhexadecan-2-ol. For example,
- The primary and secondary alcohols give a mixture of products due to a possible rearrangement of carbocation intermediate.
- The tertiary alcohol yields exclusively only one alkylated product.
- The alkylbenzenes were extensively analyzed by GC and GC-MS.

5.4] Friedel-Crafts benzylation of 1,4-dimethoxybenzenes with benzyl halide using ZnCl₂ exchanged with Montmorillonite K10:

Benzylation of p-dialkoxybenzene can be achieved through the use of modified Montmorillonite K-10 with ZnCl₂ (Clayzic).³⁰
6] Present Work

Montmorillonite K-10 Catalyzed Friedel-Crafts Benzylation with Benzyl Benzoate and Allylation with Cinnamyl Acetate:

The Friedel-Crafts reactions with carboxylic esters are not often employed. Most of the time, acylated product is formed with the esters but no alkylation has so far been achieved. As far as we know, there has not been a single report on the use of activated esters such as benzyl benzoate and cinnamyl acetate for Friedel-Crafts reactions. Herein, we wish to focus them as a versatile and attractive benzylating and allylating agents for the Friedel-Crafts reactions of electron rich aromatics.

Previously Montmorillonite K-10 was effectively used in several Friedel-Crafts alkylation reactions with various alkylating agents such as alcohols, alkyl halides and olefins. But its use in combination with benzyl benzoate and cinnamyl acetate was never before reported.

Initially, the Friedel-Crafts benzylation reaction of various aromatic compounds with benzyl benzoate was attempted using Montmorillonite K-10 as a catalyst.

\[
\begin{align*}
\text{Ph} & + \text{PhCOO} & \xrightarrow{\text{Montmorillonite K-10}} & \text{Ph} \\
\text{R} & & \text{dioxane, reflux} & \text{R} \\
\end{align*}
\]

The reaction of anisole with benzyl benzoate was chosen as a model reaction for our study. A mixture of anisole (10 mmoles), benzyl benzoate (10 mmoles) and Montmorillonite K-10 (500 mg) was refluxed in dioxane (20 ml) for half an hour. The reaction proceeded successfully and monobenzylated product was indeed formed. The reaction stops with monobenzylaation and does not proceed for the formation of di- or poly-benzylated products.
Having succeeded with benzyl benzoate, the reaction was investigated for cinnamyl acetate for the Friedel-Crafts allylation reactions. As anticipated, the allylated products were obtained but in the moderate yields.

\[
\begin{align*}
R\text{H} & + \text{Ph} & \xrightarrow{\text{Montmorillonite K-10}} & \text{Ph} \\
\text{dioxane, reflux} & & & \text{R}\end{align*}
\]

In this Friedel-Crafts benzylation and allylation, benzoic acid and acetic acid will be liberated as the side products. So after the completion of the reaction, the mixture was washed with 10 % NaHCO₃, particularly to remove benzoic acid.

The reaction conditions such as the choice of the solvent, reaction time and the temperature were, then, examined in detail.
7] Results and Discussion:

The general attributes of this methodology were studied by subjecting severally substituted benzene to benzylation and allylation reactions. The results are summarized in Table 1 and 2.

**Alkyl Benzene:**

The moderately activated alkyl benzenes such as toluene, o-xylene, m-xylene and p-xylene were subjected to benzylation and allylation reactions. The corresponding alkylated products were obtained in good to excellent yields. However a mixture of ortho and para in 1:3 proportion of the alkylated product was formed in case of toluene. This is supported by the measurement of integration heights of the signals in $^1$H NMR spectra of benzylated product of toluene.

```
\[
\text{Ph} + \text{Ph} + \text{Ph} \xrightarrow{\text{Montmorillonite K-10, dioxane, reflux}} \text{Ph}\text{Ph} + \text{Ph}\text{Ph}
\]
```

However, in the cases of ortho, meta and para- xylene, only one benzylated product is formed.

All the reactions mentioned in Table 1 and 2 were carried out in dioxane as a solvent. But in case of Friedel-Crafts reactions of alkyl benzene, the substrate itself can be used as a solvent. We have carried out this practice, particularly, for alkyl benzene such as toluene, ortho, meta, and para xylene. The yields obtained under these conditions were far better than that of dioxane as a solvent for Friedel-Crafts reactions. This is partly attributed to the possible complexation of Montmorillonite K-10 with oxygen lone pair of dioxane. The yields are compared in the following table for the solvent dioxane and the substrate itself as a solvent.
In all the above reactions, the mixture was refluxed for five hours and the reactions were monitored with respect to the consumption of activated esters.

**Alkoxybenzene:**

The highly activated methoxy benzene such as anisole, 1,3-dimethoxybenzene and hydroquinone dimethyl ether underwent benzylation and allylation in excellent yields (75-88%) with the reaction time of less than two hour. The anisole has yielded a mixture of ortho and para benzylated as well as allylated product roughly in a 1:3 proportion. In case of 1,3-dimethoxybenzene and hydroquinone dimethyl ether, only one alkylated product is formed. The electron density of aromatic ring was shown to have considerable effect on the yield and time of reaction. The reaction time was shorter and the yields were higher in quantity for methoxy benzene compared to the moderately activated alkyl benzene.

**Phenols:**

It is remarkable that phenols undergo nuclear benzylation/allylation rather than O-alkylation under the reaction conditions. In case of phenol, a mixture of ortho and para C-alkylated product is formed. This is in contrast to the previously reported method.\textsuperscript{15}
Deactivated Arenes:

The deactivated arenes such as nitrobenzene, bromobenzene and chlorobenzene were failed to undergo Friedel-Crafts benzylaion and allylation even after refluxing for 24 hours.

In all the Friedel-Crafts reactions of arenes, there is no formation of poly-benzylation / allylation products. No side products were obtained from the isomerization of double bond in allylation reaction.
Table 1: Benzylation of arenes with Benzyl Benzoate Catalysed by Montmorillonite K-10

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Arenes</th>
<th>Benzylation Product</th>
<th>Time / h</th>
<th>Yield %α (ortho:para) β</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>MeON0</td>
<td>MeO-Ph</td>
<td>0.5</td>
<td>88 (1:3)</td>
</tr>
<tr>
<td>b</td>
<td>MeC/MeO</td>
<td>MeO-Ph</td>
<td>0.5</td>
<td>86</td>
</tr>
<tr>
<td>c</td>
<td>MeO-OMe</td>
<td>MeO-Ph</td>
<td>0.7</td>
<td>80</td>
</tr>
<tr>
<td>d</td>
<td></td>
<td>Ph</td>
<td>4.0</td>
<td>74 (1:3)</td>
</tr>
<tr>
<td>e</td>
<td></td>
<td>Ph</td>
<td>3.0</td>
<td>77</td>
</tr>
<tr>
<td>f</td>
<td></td>
<td>Ph</td>
<td>3.0</td>
<td>80</td>
</tr>
<tr>
<td>g</td>
<td></td>
<td>Ph</td>
<td>3.0</td>
<td>76</td>
</tr>
<tr>
<td>h</td>
<td>MeO</td>
<td>Ph</td>
<td>1.0</td>
<td>81</td>
</tr>
<tr>
<td>i</td>
<td>HO-Ph</td>
<td>Ph</td>
<td>2.0</td>
<td>82 (1:3)</td>
</tr>
<tr>
<td>j</td>
<td>HO-OMe</td>
<td>Ph</td>
<td>2.0</td>
<td>83</td>
</tr>
</tbody>
</table>

α : Yield refers to isolated products.
β : Identified by 1H NMR spectroscopy.
Table 2: Allylation of arenes with Cinnamyl Acetate Catalysed by Montmorillonite K-10

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Arenes (1)</th>
<th>Allylation Product (3)</th>
<th>Time / h</th>
<th>Yield %α (ortho:para)β</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>MeO·</td>
<td>MeO·</td>
<td>1.0</td>
<td>81 (1:3)</td>
</tr>
<tr>
<td>b</td>
<td>MeO·</td>
<td>MeO·</td>
<td>1.0</td>
<td>77</td>
</tr>
<tr>
<td>c</td>
<td>MeO·</td>
<td>MeO·</td>
<td>1.5</td>
<td>73</td>
</tr>
<tr>
<td>d</td>
<td></td>
<td>MeO·</td>
<td>3.0</td>
<td>69 (1:3)</td>
</tr>
<tr>
<td>e</td>
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<tr>
<td>i</td>
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<td>HO·</td>
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</tr>
<tr>
<td>j</td>
<td>HO·</td>
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<td>2.5</td>
<td>72</td>
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</table>

α: Yield refers to isolated products.

β: Identified by ¹H NMR spectroscopy.
Reaction Mechanism:

Montmorillonite K-10 is a solid acid catalyst which can function as both Bronsted and Lewis acid. It has the ability to produce carbocation as an intermediate in several organic reactions. Its Bronsted acid sites are strong enough to catalyze backbone reactions in steroids.\(^3\) Its Lewis acidity, at least as efficient as AlCl\(_3\), also promotes Friedel-Crafts reactions.\(^2\) In the following proposed mechanism for Friedel-Crafts benzylation and allylation, we have considered Montmorillonite K-10 as equivalent to proton source. The reaction mechanism of benzylation and allylation will proceed through the following three stages:

**Step I: Generation of Carbocation i.e. electrophile**

Montmorillonite K-10 (i.e. a proton) is expected to coordinate with the oxygen lone pair of carbonyl group of benzyl benzoate and cinnamyl acetate. This will promote the departure of benzoate and acetate anion with the formation of a resonance stabilized benzyl and cinnamyl carbocation respectively.

**Step II: Formation of \(\sigma\)-complex**

The potentially electrophilic benzyl and cinnamyl carbocation will attack on aromatic nucleus to form the resonance stabilized \(\sigma\)-complex.

**Step III: Aromatisation of the \(\sigma\)-complex**

Finally, the acid catalyst will be liberated via the aromatization of \(\sigma\)-complex with the formation of benzylated and allylated product.
9] Experimental Section

Unless otherwise noted, commercially available chemicals with at least 98 % purity were used throughout this study. All solvents were reagent grade and freshly distilled. Montmorillonite K-10 was purchased from Fluka and dried at 100 °C prior to use. All the organic extracts were dried over anhydrous sodium sulphate. Manually coated glass plates with silica gel were used for thin layer chromatography. Column chromatography was performed on silica gel using appropriate percentage combination of petroleum ether (60 – 80 °C) and ethyl acetate.

Typical Procedure: A mixture of arene (10 mmol), benzyl benzoate (10 mmol) or cinnamyl acetate (10 mmol) and Montmorillonite K-10 catalyst (500 mg) in dioxane (20 ml) was refluxed for the time mentioned in Table 1 and 2. The reaction was monitored by TLC. After completion of reaction, the catalyst was filtered and the filtrate was washed with 10% NaHCO₃ solution. The resulting solution was then extracted with CH₂Cl₂ (2 X 15 ml), dried over anhydrous sodium sulfate and purified by column chromatography over silica (95:5, pet ether: ethyl acetate) to give viscous colorless liquid as a final alkylated product.

Note: For alkylation of toluene, o, m and p-xylene, the substrate itself was used as a solvent (20 ml) instead of dioxane. Remaining sequence is very much similar to the above described general procedure.
10) Characterization of the products:

IR spectra were recorded on a Perkin-Elmer 137-E spectrometer. The $^1$H NMR spectra were recorded on a 300 MHz instrument and the chemical shifts were reported with TMS as an internal standard. The representative spectral analysis for few of the products is given below:

1) 4-Benzyltoluene

\[ \text{HNMR: } \delta 2.2 \text{ (3H, s)} \]
\[ 3.9 \text{ (2H, s)} \]
\[ 7.0-7.2 \text{ (9H, m)} \]

IR (cm$^{-1}$, Neat): 3024, 2972, 2921, 1602, 1531, 1453, 1029, 757, 668.

Anal. Calcd for C$_{14}$H$_{14}$: C, 93.33%; H, 7.77

Found: C, 93.18%; H, 7.65.

2) 4-Methyl-2-benzyltoluene

\[ \text{HNMR: } \delta 2.3 \text{ (3H, s)} \]
\[ 2.5 \text{ (3H, s)} \]
\[ 4.1 \text{ (2H, s)} \]
\[ 7.0-7.4 \text{ (9H, m)} \]

IR (cm$^{-1}$, Neat): 3025, 2967, 2920, 1602, 1503, 1494, 1452, 1372, 1073, 808, 725, 696.

Anal. Calcd for C$_{15}$H$_{16}$: C, 91.83%; H, 8.16

Found: C, 91.76%; H, 8.19.
3] 2-Benzyl-4-methyItoluene

\[ \text{HNMR: } \delta 2.2 \text{ (3H, s)} \]
\[ 2.4 \text{ (3H, s)} \]
\[ 4.1 \text{ (2H, s)} \]
\[ 7.1-7.4 \text{ (8H, m)} \]

IR (cm\(^{-1}\), Neat): 3018, 2923, 1601, 1494, 1216, 909, 757.

Anal. Calcd for \( \text{C}_{15}\text{H}_{16} \): C, 91.83; H, 8.16
Found: C, 91.73; H, 8.25.

4] 3-(4-Methoxyphenyl)-1-phenylpropene

\[ \text{HNMR: } \delta 3.5 \text{ (3H, s)} \]
\[ 3.8 \text{ (2H, d)} \]
\[ 6.3-6.5 \text{ (2H, m)} \]
\[ 7.1-7.4 \text{ (9H, m)} \]

IR (cm\(^{-1}\), Neat): 3010, 2961, 2915, 1625, 1458, 1210, 823, 720.

Anal. Calcd for \( \text{C}_{15}\text{H}_{16}\text{O}_2 \): C, 85.71; H, 7.14
Found: C, 85.68; H, 7.08.

5] 3-(3,4-Dimethylphenyl)-1-phenylpropene

\[ \text{HNMR: } \delta 2.1 \text{ (3H, s)} \]
\[ 2.2 \text{ (3H, s)} \]
\[ 3.6 \text{ (2H, d)} \]
\[ 6.3-6.5 \text{ (2H, m)} \]
\[ 7.0-7.5 \text{ (8H, m)} \]

IR (cm\(^{-1}\), Neat): 3010, 2952, 2938, 1633, 1426, 1280, 1024, 872, 653.

Anal. Calcd for \( \text{C}_{17}\text{H}_{18} \): C, 91.89; H, 8.10
Found: C, 91.72; H, 8.07.
6] 3-(2-Methyl-4-methoxyphenyl)-1-phenylpropene

$^1$HNMR:  δ 2.3 (3H, s)  
3.5 (2H, d)  
3.6 (3H, s)  
6.2-6.4 (2H, m)  
6.8-7.5 (8H, m)  

IR (cm$^{-1}$, Neat):  3067, 2954, 2847, 1634, 1151, 1017, 780.  

Anal. Calcd for C$_{17}$H$_{18}$O:  C, 85.79; H, 7.56  
Found:  C, 85.78; H, 7.54.
Peptide: 

\[
\text{Bhosale} \quad \text{Sample: KB} \\
\text{Date: 10/7/01} \\
\text{Comment: CHCl3}
\]

Wavenumbers:

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Diagram: 3:1 ratio of two molecules.
**Table: NMR Parameters**

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</table>

**Diagram:**

- Compound structure: \( \text{CH}_3 \text{Ph} \)
- Peaks at 9.00, 2.44, 7.54 ppm

**Comment:**

- JADHAV V.H/EXP-KC/CDCL3
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The spectrum shows a chemical structure with peaks at 9.00, 2.28, and 8.12 ppm. The chemical is identified as chloroform-

\[ \text{H}_3\text{C} - \text{Ph} \]
H3C

Ph

H3C

Peak Report
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Name: Bhorade
Sample: Pr Lu,
Date: 12/7/01
Comment: CHC3
11) Merits of the methodology and conclusion:

Following are the important merits associated with the Montmorillonite K-10 catalyzed Friedel-Crafts benzylation and allylation with activated esters.

1. The first time use of benzyl benzoate and cinnamyl acetate as alkylating agents is an attractive feature of the methodology.

2. The Friedel-Crafts benzylation and allylation stops at mono-alkylation stage i.e. no poly-alkylation.

3. In Friedel-Crafts allylation reaction, no side products are formed from the isomerization of double bond.

4. Use of environmentally benign and cheap Montmorillonite K-10 catalyst for Friedel-Crafts reaction.

5. The catalyst can be simply filtered off on completion of reaction.

6. Economically viable, rapid and high yielding protocol.

Conclusion:

In conclusion Friedel-Crafts reactions mediated by Montmorillonite K-10 using unconventional alkylating substrates like benzyl benzoate and cinnamyl acetate provide a viable route synthesize valuable fine chemicals. Furthermore, this method is advantageous because of easy separation, consistent yield and minimum environmental effects.
12 References:


