



## Review on Friedel-Crafts acylation of benzene derivatives using various catalytic systems

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### Abstract

This review covers the Friedel-Craft's acylation of benzene derivatives using various catalysts such as metal halogen acid, metal oxide, metal triflate, ionic liquids and miscellaneous catalytic systems. The author tries to cover all the literature in this area. Some of the methods described above are useful in organic synthesis, which is of great important synthesis in the preparation of natural products, active pharmaceutical ingredients, agrochemicals, fine chemicals and fragrances.

**Keywords:** Friedel-Craft's acylation, Lewis acid, catalytic systems, metal oxide, ionic liquids, metal triflate, acid chloride, acid anhydride

### Introduction

One of the major goals of modern synthetic organic chemical research is to provide new methodology and reagents that facilitate the synthesis of highly complex carbon-containing molecules, particularly those that might have biological activity or can be incorporated into materials with unique behavior. The invention of new routes to access small molecule substrates for synthesis, and perhaps as targets themselves, is required to satisfy demands for high yields and to maximize molecular diversity. The ability to manipulate or modify substrates containing a variety of functional groups can simplify a synthetic sequence and improve overall product yields. Friedel-Crafts acylation of aromatic compounds is one of the most frequently used reactions in organic synthesis to form C-C bonds, which is of great importance in the preparation of natural products, active pharmaceutical ingredients, agrochemicals, fine chemicals and fragrances<sup>[1-4]</sup>.

Unfortunately, the traditional Lewis acid-catalyzed Friedel-Crafts acylation has its environmental drawbacks, including requiring more than stoichiometric amounts, strictly anhydrous conditions, and produces corrosive acid wastes. Herein, the author summarizes the Friedel-Craft's acylation of benzene and substituted benzene compounds using various catalytic systems as follows.

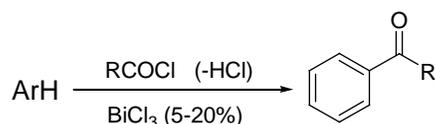
### Metal halogen acid-Lewis acid Based Catalyst

Electrophilic aromatic substitution allows the synthesis of monoacylated products from the reaction between arenes and acyl chlorides or anhydrides. The products are deactivated, and do not undergo a second substitution. Normally, a stoichiometric amount of the Lewis acid catalyst is required, because both the substrate and the product form complexes.

Lewis-acid (LA)-catalyzed reactions are of great interest because of their unique reactivities and selectivities and mild reaction conditions used<sup>[5]</sup>. Lewis acid catalysis of organic reactions, a metal-based Lewis acid acts as an electron pair acceptor to increase the reactivity of a substrate. Common Lewis acid catalysts are based on main group metals such as aluminum, boron, silicon and tin, as well as many early

(titanium, zirconium) and late (iron, copper, zinc) d-block metals. Early developments in Lewis acid reagents focused on easily available compounds such as  $\text{TiCl}_4$ ,  $\text{BF}_3$ ,  $\text{SnCl}_4$ , and  $\text{AlCl}_3$ . Over the years, versatile catalysts bearing ligands designed for specific applications have facilitated improvement in both reactivity and selectivity of Lewis acid-catalyzed reactions. Metal halogen acid catalyzed Friedel-Craft's acylation reactions of benzene and substituted benzene are described as below.

Christophe Le Roux *et al.*<sup>[6]</sup> carried out the Friedel-Crafts acylation of activated and polycyclic aromatics by using the catalyst bismuth (III) chloride which is generated in situ from bismuth (III) oxychloride, a water insensitive and eco-friendly material. Bismuth (III) oxychloride is easily recovered in near quantitative yields after an aqueous work-up. In addition, in this method  $\text{BiOCl}$  was recycled by in situ transformation into  $\text{BiCl}_3$  using the acylating agent, acid chloride, or before the acylation reaction using thionyl chloride. This added advantage of this recovery method makes this method applicable to most of the known  $\text{BiCl}_3$ -catalyzed organic reactions. Even though the catalytic power of  $\text{BiCl}_3$  is limited; this method is a simple, cheap, safe and eco-friendly alternative to the classical processes of the FC acylation and related reactions (**Scheme-1**).

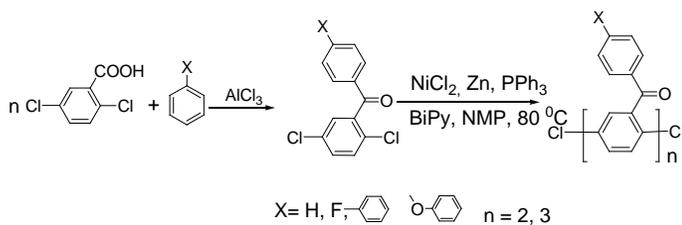


Ar = Toluene, mesitylene, o-xylene, m-xylene, p-xylene, anisole  
R = Ph,  $\text{Me}(\text{CH}_2)_4$ ,  $\text{Me}(\text{CH})$ ,  $\text{p-NO}_2\text{C}_6\text{H}_4$ ,  $\text{Me}_2\text{C}$  etc.

**Scheme-1:** Synthesis of polycyclic aromatics using bismuth (III) chloride.

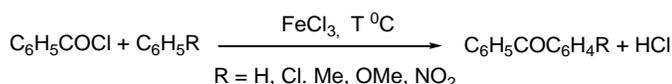
Hossein Ghassemi *et al.*<sup>[7]</sup> reported the synthesis of several substituted poly(2,5-benzophenone)s and their copolymers. The monomers were prepared by Friedel-Crafts catalyzed reaction of 2,5-dichlorobenzoyl chloride and several aromatic compounds.

These polymers were chemically modified for the potential applications. The results further demonstrate the feasibility of synthesizing aryl-substituted poly (2,5-benzophenone)s via Ni(0)-catalyzed coupling polymerization (Scheme-2).



**Scheme 2:** Synthesis of polymers using monomers prepared by Friedel-Crafts acylation.

Jean-Fran Gois Scutto., *et al.*,<sup>[8]</sup> synthesized series of benzene derivatives by the acylation of benzene (and deactivated aromatics) with little Lewis acid catalyst will give acceptable yields if both a moderately active catalyst ( $\text{FeCl}_3$ ,  $\text{ZnCl}_2$ ) a high temperature of reaction are used (Scheme-3).



**Scheme 3:** Friedel-Crafts acylation of benzene and deactivated benzene with  $\text{FeCl}_3$ .

### Metal Triflate Catalyst

Metal trifluoromethane sulfonates (metal triflates) are a class of green homogeneous acidic catalysts, which have been efficiently employed in a number of chemical processes, including valorisation of polysaccharides. These catalysts are able to selectively promote Lewis acid catalysed reactions, or Brønsted acid catalysed processes through Lewis acid-assisted Brønsted acidity<sup>[9]</sup>. Metal triflates have been used in a wide variety of synthetic organic transformations and offer an efficient, environmentally friendly alternative to traditional Lewis acids. Metal triflates can typically be recovered and reused without loss of catalytic activity. Reactions catalyzed by metal triflates range from various C-C bond-forming reactions, such as Friedel-Crafts acylation and alkylation to C-N bond-forming reactions and others.

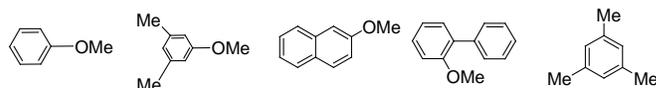
The most characteristic feature of  $\text{Ln}(\text{OTf})_3$  is that they are stable and work as Lewis acids in water. After the first report, not only  $\text{Ln}(\text{OTf})_3$  ( $\text{Ln}$ ) La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) but also scandium (Sc) and yttrium (Y) triflates were shown to be water-compatible Lewis acids, and these rare-earth metal triflates [ $\text{RE}(\text{OTf})_3$ ] have been regarded as new types of Lewis acids. Many useful reactions are catalyzed by rare-earth metal triflates in aqueous media. Only catalytic amounts of the triflates are enough to complete the reactions in most cases. Furthermore, rare-earth metal triflates can be recovered easily after reactions and reused without loss of activity. Useful organic transformations employing rare-earth metal triflates as Lewis acid catalysts are discussed below.

Jianliang Xiao *et al.*,<sup>[10]</sup> have carried out the aromatic electrophilic substitution reactions such as benzylation and acetylation catalyzed by metal triflates have been conducted in an ionic liquid,  $[\text{bmim}][\text{BF}_4]$  ( $\text{bmim}$ =1-butyl-3-methylimidazolium).

$\text{Cu}(\text{OTf})_2$  ( $\text{OTf}$  = trifluoromethanesulfonate) was found to be the most efficient catalyst used, affording quantitative conversion of benzoyl chloride and anisole to methoxybenzophenone within 1 h and with an *ortho/para* product ratio (*o/p*) of 4/96. The same reaction performed in the molecular solvents  $\text{CH}_3\text{CN}$  and  $\text{CH}_2\text{ClCH}_2\text{Cl}$  gave lower 1 h conversions of 64 and 73%, respectively, and a reduced *o/p* regioselectivity of 7/93 in both cases. The scope and limitations of the reaction and recyclability of the ionic liquid/catalyst system are presented (Scheme-4).



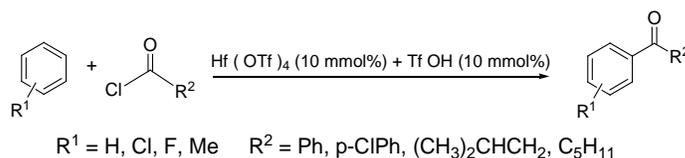
Where Ar-H



Where R = Ph, Me,  $\text{C}_2\text{H}_5$ ,  $\text{C}_6\text{H}_{13}$  X = R = Ac, PhCO,  $\text{C}_2\text{H}_5\text{CO}$ ,  $\text{C}_6\text{H}_{13}$

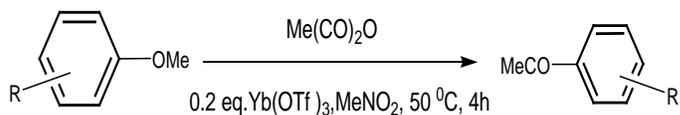
**Scheme 4:**  $\text{Cu}(\text{OTf})_2$  catalysed acylation of aromatic compounds in  $[\text{bmim}][\text{BF}_4]$ .

Shu Kobayashi *et al.*,<sup>[11]</sup> reported the Friedel-Crafts acylation of benzene and unactivated benzenes such as chlorobenzene, and fluorobenzene in the presence of catalytic amounts of hafnium(IV)triflate ( $\text{Hf}(\text{OTf})_4$ ) and trifluoromethanesulfonic acid ( $\text{TfOH}$ ). They found that combination of  $\text{Hf}(\text{OTf})_4$  and  $\text{TfOH}$  accelerated the catalytic Friedel-Crafts acylation of benzene dramatically. Both aromatic and aliphatic carboxylic acid chlorides reacted smoothly under the conditions to afford the corresponding aromatic ketones in good yields (Scheme-5).



**Scheme 5:** Friedel-Crafts acylation of benzene and unactivated benzenes such as chlorobenzene, and fluorobenzene in the presence of catalytic amounts of hafnium (IV) triflate ( $\text{Hf}(\text{OTf})_4$ ) and trifluoromethanesulfonic acid ( $\text{TfOH}$ ).

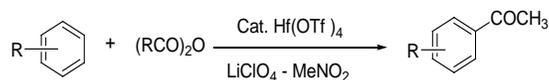
Atsushi Kawada *et al.*,<sup>[12]</sup> reported the Lanthanide triflate catalysed Friedel-Crafts acylation of substituted benzenes proceeds using a catalytic amount of a lanthanide trifluoromethanesulfonate [ $\text{Ln}(\text{OTf})_3$ ], which is easily recovered from the reaction mixture and reused without a decrease in catalytic activity. Among all the Lanthanide triflate catalyst used 0.2 eq.  $\text{Yb}(\text{OTf})_3$  gives excellent yield of 93% (Scheme-6).



R = OMe, NMe,  $\text{NMe}_2$ ,  $\text{CMe}_2$ ,  $\text{CMe}_3$

**Scheme 6:** Lanthanide triflate catalyzed Friedel-Crafts acylation of substituted benzenes.

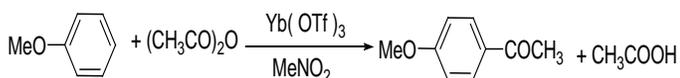
Shu Kobayashi *et al.*,<sup>[13]</sup> performed the catalytic Friedel-Crafts acylation reactions of substituted benzenes with acid anhydrides were successfully carried out by using Hf(OTf)<sub>4</sub> as a catalyst. Among the various catalytic systems used in the reaction, they found that the turnover of Lewis acid catalysts in the Friedel-Crafts acylation is 10-20 times improved in lithium perchlorate-nitromethane (LiClO<sub>4</sub>- MeNO<sub>2</sub>) (Scheme-7).



R = OCH<sub>3</sub>, 1, 2-dimethyl, 1, 3-dimethyl, 1, 4-dimethyl, 1, 2-dimethoxy, H, 1, 3, 5-trimethyl  
R = CH<sub>3</sub>, (CH<sub>3</sub>)<sub>2</sub>CH, C<sub>6</sub>H<sub>5</sub>, (CH<sub>3</sub>)<sub>3</sub>C

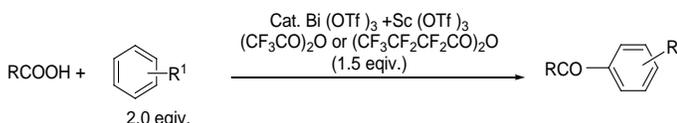
**Scheme 7:** Hf(OTf)<sub>4</sub> catalyzed Friedel-Crafts acylation reactions of substituted benzenes with acid anhydrides.

Tobin J. Marks *et al.*,<sup>[14]</sup> investigated Lanthanide trifluoromethane sulfonates, Ln(OTf)<sub>3</sub> (OTf-trifluoromethane sulfonate), serve as effective precatalysts for the rapid, regioselective, intermolecular acylation of activated arenes. This contribution probes mechanism and metal ionic radius effects in the catalytic lanthanide triflate-mediated acylation of anisole with acetic anhydride. Kinetic studies of Ln(OTf)<sub>3</sub> (Ln = La, Eu, Yb, Lu)-mediated anisole acylation with acetic anhydride in nitromethane reveal that, the observed primary kinetic isotope effect of  $k_H/k_D$  ) 2.6 ( 0.15 is consistent with arene C-H bond scission in the turnover-limiting step. The proposed catalytic pathway involves precatalyst formation via interaction of Ln(OTf)<sub>3</sub> with acetic anhydride, followed by Ln<sup>3+</sup>-anisole  $\pi$ -complexation, substrate-electrophile  $\sigma$ -complex formation, and turnover limiting C-H bond scission. Lanthanide size effects on turnover frequencies are consistent with a transition state lacking significant ionic radius-dependent steric constraints. Substrate-Ln<sup>3+</sup> interactions using paramagnetic Gd<sup>3+</sup> and Yb<sup>3+</sup> NMR probes and factors affecting reaction rates such as arene substituent and added LiClO<sub>4</sub> co catalyst are also explored (Scheme-8).



**Scheme 8:** Lanthanide trifluoromethanesulfonates Ln(OTf)<sub>3</sub> acylation of anisole with acetic anhydride.

Yoh-ichi Matsushita *et al.*,<sup>[15]</sup> synthesized aromatic ketones by solvent less Friedel-Crafts acylation of anisole, mesitylene, xylenes, and toluene with acetic acid and benzoic acid in the presence of trifluoroacetic anhydride by use of bismuth or scandium triflate at 30 °C. Toluene, benzene, and even deactivated substrate such as chlorobenzene were benzoylated by the combined use of heptafluorobutyric anhydride and bismuth triflate at 75–100 °C. The catalyst could be easily recovered and reused repeatedly for the reaction (Scheme-9).



**Scheme-9:** Synthesis aromatic ketones by solvent less Friedel-Crafts acylation.

## Metal oxide catalyst

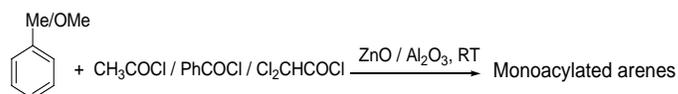
Metal oxides represent one of the most important and widely employed categories of solid catalysts, either as active phases or as supports. Metal oxides are utilized both for their acid-base and redox properties and constitute the largest family of catalysts in heterogeneous catalysis<sup>[16]</sup>. Metals and metal oxides form the bulk of catalysts employed for many synthetic conversions. Transition and noble group metals are frequently used as catalysts and their activity has been attributed to the outer electron configuration<sup>[17]</sup>. Metal oxide catalyzed Friedel craft's acylation of benzene and substituted benzene are given below. Hashem Sharghi *et al.*,<sup>[18]</sup> reported a rapid Friedel Crafts acylation of a range of activated and unactivated aromatic compounds such as anisole and chlorobenzene with acid chlorides in solvent-free conditions at room temperature using zinc oxide (ZnO). The ZnO powder can be reused up to three times after simple washing with dichloromethane (Scheme-10).



**Scheme 10:** Friedel-crafts acylation of substituted benzene with acid chloride using ZnO catalyst.

Reactionson a Solid Surface. A Simple, Economical and Efficient Friedel-Crafts Acylation Reaction over Zinc Oxide (ZnO) as a New Catalyst.

Kartik Kumar Nandi *et al.*,<sup>[19]</sup> reported a simple, efficient, and green procedure developed for mono-acylation of arenes with acid chlorides/dichloroacetylchloride over zinc oxide in 2:1:2 molar ratios at room temperature. Selective monoacylations in mild reaction conditions and recycling of recovered catalyst are notable green features and advantages of this method (Scheme-11).



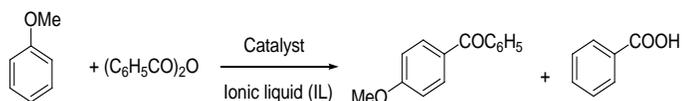
**Scheme 11:** Green synthesis of monoacetylated arenes.

## Ionic liquid catalyst

Ionic liquids are attracting a great deal of attention as possible replacement for conventional molecular solvents for catalytic and organic reactions. They complete the use of environmentally friendly water, supercritical fluids or perfluorinated solvents. Features that make ionic liquids attractive include their lack of vapor pressure and the great versatility of their chemical and physical properties. By a judicious combination of cations and anions, it is possible to adjust the solvent properties to the requirement of the reactions, thus creating an almost indefinitely set of "designer solvents". Besides the possibility of recycling the catalytic system, one main potential interest in using ionic liquids results in the unique interactions of these media with the active species and in the possibility to modify the reaction activity and selectivity. Their successful use as solvents has been demonstrated for a wide range of organic reactions including acid

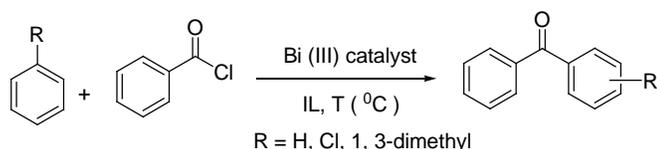
catalyzed reactions and transition metal catalyzed transformations<sup>[20]</sup>.

Christopher Hardacre *et al.*,<sup>[21]</sup> reported, the comparison of three ionic liquid-mediated catalytic processes for the benzoylation of anisole with benzoic anhydride is presented. The predominant activity is associated with the in situ formation of a homogeneous acid catalyst, the low cost and facile separation of the zeolite-catalysed process leads to this route being the most economically viable overall option. The results of a continuous flow miniplant based on the zeolite catalyst are also presented and compared with the reaction using a small plug flow reactor (Scheme-12).



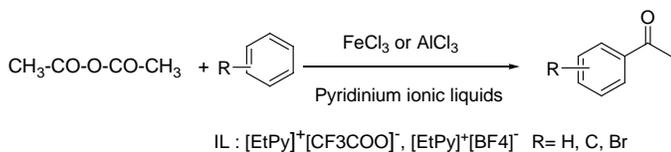
**Scheme 12:** Ionic liquid-mediated catalytic processes for the benzoylation of anisole with benzoic anhydride.

Michel Vaultier *et al.*,<sup>[22]</sup> studied the activity of four bismuth (III) derivatives when employed as Friedel–Crafts catalysts for the acylation of aromatics was found to increase dramatically when dissolved in ionic liquids. Solutions of bismuth oxide or triflate in [emim][NTf<sub>2</sub>] and [bmim][NTf<sub>2</sub>] are the most efficient catalytic systems, with catalyst loading as low as 1% leading to clean, high-yielding acylation of a variety of benzene derivatives. These improved Friedel–Crafts catalytic systems can also be efficiently recycled as opposed to traditional systems (Scheme-13).



**Scheme 13:** Friedel-Crafts acylation of benzene derivatives Bi(III) triflate in ionic liquid.

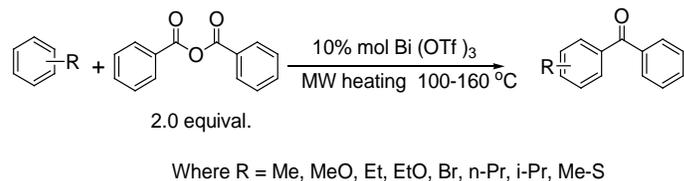
Sanjay V. Malhotra *et al.*,<sup>[23]</sup> investigated the Friedel-Crafts acylations of aromatic compounds with acetic anhydride in pyridinium based ionic liquids (ILs). The effect of factors such as reactant composition, catalyst-IL composition, catalyst dosage and reaction temperature were studied. The reactions were found to proceed under relatively mild conditions with excellent conversions; and a simple product isolation procedure was achieved. ILs could also be recycled and reused effectively, thus rendering green characteristic to this reaction (Scheme-14).



**Scheme 14:** Friedel-Crafts acylations of aromatic compounds with acetic anhydride in pyridinium based ionic liquids (ILs).

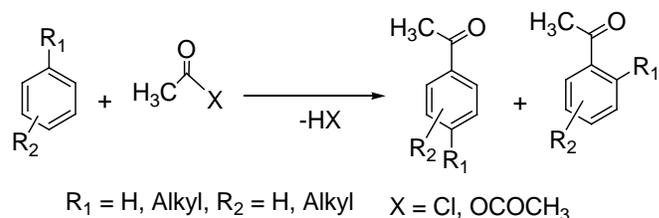
Phuong Hoang Tran *et al.*,<sup>[24]</sup> investigated an efficient and facile bismuth trifluoromethanesulfonate catalyzed benzoylation of aromatic compounds using benzoic anhydride under solvent-free microwave irradiation has been developed. The microwave-

assisted Friedel-Crafts benzoylation results in good yields within short reaction times. Bismuth triflate is easily recovered and reused for several times without significant loss of catalytic activity (Scheme-15).



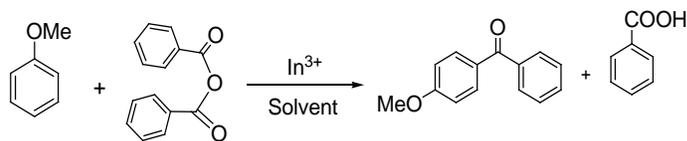
**Scheme 15:** Bi(OTf)<sub>3</sub> catalyzed Friedel-Crafts acylation of aromatic compounds under microwave irradiation.

W.F. Holderich *et al.*,<sup>[25]</sup> reported and discussed use of different ionic liquids catalysts for Friedel-Crafts acylation reactions. Supported chloroferrate ionic liquids were tested in liquid and in gas phase reactions. The catalysts, consisting of the ionic liquid and charcoal as a carrier, are easy to prepare and show interesting catalytic properties. Comparisons between different ionic liquids in the liquid phase are presented, as well as reactions in the gas phase (Scheme-16).



**Scheme 16:** Friedel-Crafts acylation of Benzene derivatives with acetic anhydride or acetyl chloride using ionic liquid catalyst.

Martyn J. Earle, *et al.*,<sup>[26]</sup> described the Chloroindate (III) ionic liquids are versatile reaction media for Friedel-Crafts acylation reactions; the system is catalytic and totally recyclable, using an aqueous workup, with no leaching of the indium into the product phase (Scheme-17).

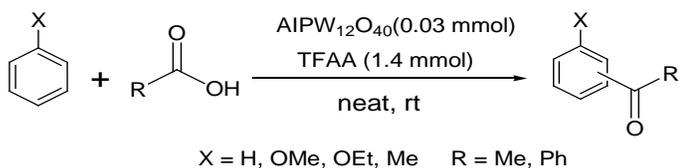


**Scheme 17:** Chloroindate (III) ionic liquids Catalyzed by Friedel-Crafts acylation.

### Miscellaneous catalytic systems

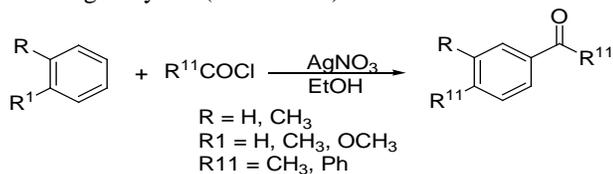
Friedel craft's acylation of benzene and substituted benzene carried out using various miscellaneous (uncategorized) catalysts are given as below.

Habib Firouzabadi *et al.*,<sup>[27]</sup> reported the use of heteropolyacids aluminum dodecatungstophosphate (AIPW12O40) as a stable and effective heterogeneous catalyst (3 mol%) for the efficient acylation of aromatic compounds using carboxylic acids in the presence of trifluoroacetic anhydride (TFAA) under mild reaction conditions in the absence of solvent (Scheme-18).



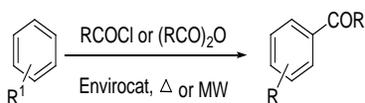
**Scheme 18:** Acylation of aromatic compounds with carboxylic acids catalyzed by AIPW<sub>12</sub>O<sub>40</sub> in the presence of trifluoroacetic anhydride.

K. M. Lokanatha Rai *et al.*,<sup>[28]</sup> investigated the Friedel–Crafts acylation of benzene derivatives such as anisole, toluene, and xylene has been successively carried out using silver nitrate as the catalyst in the presence of an eco friendly solvent (ethyl alcohol). Both benzoyl chloride and acetyl chloride reacted smoothly under the conditions to afford the corresponding ketones in good yield (Scheme-19).



**Scheme 19:** Acylation of benzene derivatives catalyzed by AgNO<sub>3</sub> in the presence of ethanol.

Babasaheb P. Bandgar *et al.*,<sup>[29]</sup> carried out the Friedel–Crafts acylation reactions of substituted benzenes with acid chloride or anhydrides in the presence of a catalytic amount of novel solid-supported reagents. The reaction proceeds smoothly with these catalysts and these catalysts are reusable and environmentally friendly (Scheme-20).



R = CH<sub>3</sub>, Ph, ClCH<sub>2</sub>, CH<sub>3</sub>CO, R<sup>1</sup> = H, CH<sub>3</sub>, OMe, Cl, OH, 1, 3-dimethoxy, 1,3,5-trimethyl

**Scheme-20:** Friedel–Crafts acylation of benzene derivatives using novel solid supported reagents.

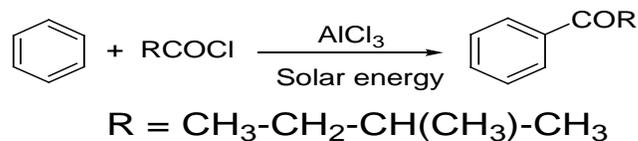
Iliyan Ivanov *et al.*,<sup>[30]</sup> have been synthesized number of aminobenzophenones by acylation of benzene and its derivatives with different 2-, 3-, 4-aminobenzoic and 4-aminophenylacetic acids in polyphosphoric acid via Friedel–Crafts reaction as compounds with expected antitumor activity (Scheme-21).



**Scheme 21:** Synthesis of number of aminobenzophenones by acylation of benzene and its derivatives with different 2, 3, 4-aminobenzoic and 4-aminophenylacetic acids in polyphosphoric acid.

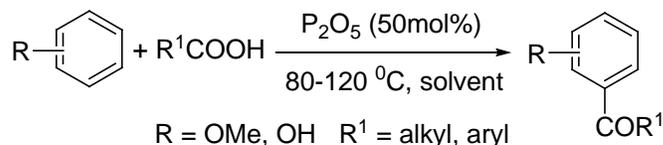
Daniel J. Swartling *et al.*,<sup>[31]</sup> have attempted to make more environmentally friendly chemical synthesis procedures. They synthesized isobutyrophenone, which is synthesized through a

Friedel–Crafts acylation of benzene using the solar reflector (Scheme-22).



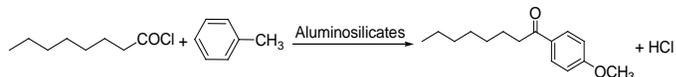
**Scheme 22:** Green synthesis of isobutyrophenone by Friedel–Crafts acylation of benzene using solar reflector.

Arumugam Sudalai *et al.*,<sup>[32]</sup> reported the liquid-phase acylation of activated aromatic substrates with aromatic and aliphatic carboxylic acids as acylating source giving aromatic ketones (45–93%) in a regioselective manner using P<sub>2</sub>O<sub>5</sub> catalyst, has been found to be a highly efficient and environmental friendly catalyst. Both. The process is particularly demonstrated at 100 g scale in the case of anisole and acetic acid to produce 4-methoxyacetophenone (Scheme-23).



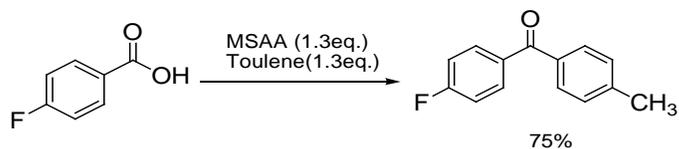
**Scheme-23:** Acylation of activated aromatic substrates with aromatic and aliphatic carboxylic acids using P<sub>2</sub>O<sub>5</sub> catalyst.

Chung-Yuan Mou *et al.*,<sup>[33]</sup> demonstrated the Friedel–Crafts acylation of aromatics. High conversion (>90%) and high selectivity (100%) using Ultrastable acidic mesoporous aluminosilicates (MCM-48-S, MCM-48-SH, MCM-41-S) with mesostructures, strong acidity, and high hydrothermal stability was synthesized from assembly of cetyltrimmonium bromide (CTAB) and pre-formed zeolite Beta seed (Scheme-24).



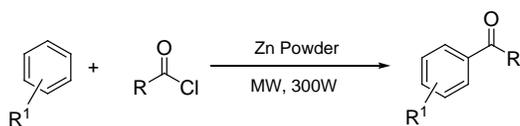
**Scheme 24:** Acylation of aromatics such as toluene with octylchloride using mesoporous aluminosilicates catalyst.

Mark C. Wilkinson., *et al.*,<sup>[34]</sup> reported a novel methodology for Friedel–Crafts acylation reactions, which allows the preparation of various aryl ketones with minimal waste containing no halogenated or metallic components, clearly differentiating it from other methodologies. The reactions precedes on the parent carboxylic acids via 1.3 equiv of a activating agent (methanesulfonic anhydride) and as little as 1.3 equiv of an aromatic nucleophile, with in general no additional solvent (Scheme-25).



**Scheme 25:** Preparation of various aryl ketones using Methanesulphonic anhydride catalyst.

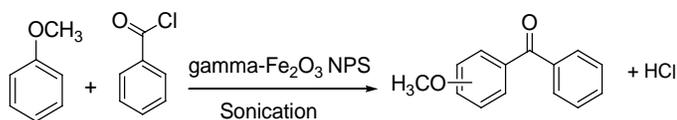
Rajive Gupta *et al.*,<sup>[35]</sup> have described a novel and highly efficient microwave-induced solvent-free protocol for Friedel–Crafts acylation of aromatic compounds using non-toxic and inexpensive Zn powder. The Zn powder can be re-used up to six times after simple washing with diethyl ether and dilute HCl. The advantages of this environmentally benign and safe protocol include a simple reaction set-up not requiring specialized equipment, high product yields, short reaction times, and the elimination of solvents or solid support. Moreover, the activated aromatic substrates give the para-isomer as the major product (Scheme-26).



R = CH<sub>3</sub>, R<sup>1</sup> = NH<sub>2</sub>, OCH<sub>3</sub>, CH<sub>3</sub>, Cl, OH, 1, 2-dihydroxy, 1, 3-dihydroxy etc.

**Scheme 26:** Microwave-Induced Synthesis of Acylated Ketones Using Zn Powder (Power = 300 W).

P. Hoang Tran *et al.*,<sup>[36]</sup> given a simple, facile and efficient method has been developed for the Friedel–Crafts benzylation of arenes using magnetic  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles (NPS) under solvent-free sonication. The  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles were used as an efficient and magnetically recoverable catalyst for the synthesis aromatic ketones in good to excellent yields at room temperature under solvent-free. The reaction occurred with high regioselectivity under mild condition. The magnetic  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles are economically synthesized in large-scale, easily separated from the reaction mixture by an external magnet and able to be reused several times without significant loss of the catalytic performance, which make them easy application to industrial processes (Scheme-27).



**Scheme-27:** Friedel crafts acylation of arenes using  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles (NPS) under solvent-free sonication.

## Conclusion

The author made a sincere effort to his best to describe the Friedel crafts acylation of benzene and substituted benzene done using various catalytic systems. Recent progress in this area replaces the water intolerable Lewis acids by the water tolerable catalyst. This article may be useful for the development of new catalyst for the Friedel crafts acylation reaction.

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