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RECENT ADVANCES IN FRIEDEL- CRAFTS REACTION

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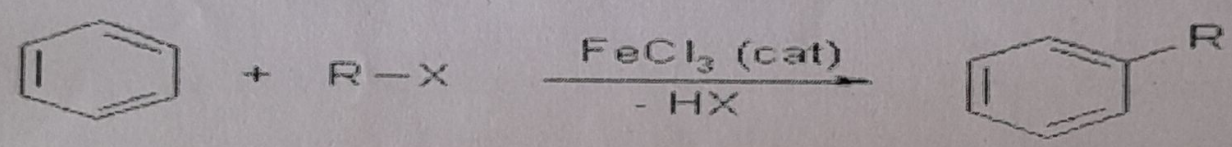
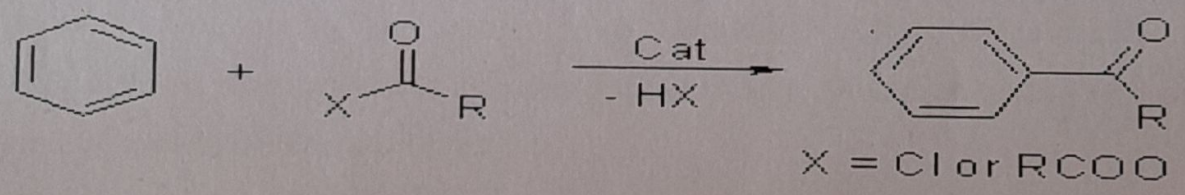
I INTRODUCTION

Among the several name reactions in organic chemistry Friedel-Crafts reaction have been extensively employed for synthesizing new organiccompounds.In 1877, Charles Friedel and James Crafts developed this reaction to attach substituents to aromatic ring.Friedel–Crafts reactions are of two main types: alkylation reactions and acylation reactions. Both proceed by electrophilic aromatic substitution.AlCl3-catalysed preparation of toluene was among the earliest examples of Friedel–Crafts alkylation, in which a hydrogen atom is substituted for an alkyl group on benzene[1].





Since several decades'Friedel crafts reactions are considered in forming new C-C bond involving aromatic moiety.FC alkylation comprises the alkylation of an appropriate aromatic ring using an alkyl halide, conventionally in the presence of a strong Lewis acid as the catalyst.[2] Commonly, anhydrous ferric chloride is used as a catalyst, in which the alkyl group initially attaches itself to the former site of the chloride ion.[3]

The FC acylation reaction is actually the acylation of certain aromatic compounds. For the FC acylation reaction, acyl chlorides are used as common acylating agents. The reaction conditions for the FC acylation reaction are exactly as same as those for FC alkylation. It is worthwhile to know that the FC acylation reaction shows several advantages over the alkylation variant. Because of the electron-withdrawing nature of the carbonyl motif, the product, which is actually a ketone, is expectedly less reactive than the substrate, thus undesired multiple acylations do not take place.[4]

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Advances in Friedel–Crafts reactions

Recent works on the advances in Friedel–Crafts acylations with special importance to organic synthesis covering the developments of methodologies with green and sustainable catalysts are remarkable. Friedel–Crafts acylation is one of the most fundamental unit processes to provide C—C bond and also to incorporate carbonyl functionality into wide varieties of substrates, e.g., aromatics, heterocycles, organo-metallics, etc. But in the era of sustainable environment, the conventional processes were less acceptable in terms of atom economy, overconsumption of toxic catalyst [e.g., AlCl3], etc. Thus, chemists are trying for greener catalytic routes that will be more eco-friendly in nature.

NandiK K (2018) developed a simple, efficient, and green procedure for mono-acylation of arenes/ferrocene/1-methylindolewith acid chlorides/dichloroacetylchloride over zinc oxide in 2:1:2 molar ratios at room temperature.Acylation reactions of toluene, anisole, 1-methylindole, and Ferrocenes were performed successfully with dichloroacetylchloride as the acylating agent and ZnO/Al2O3 as a catalyst in 2:1:2 molar ratio. Selective monoacylations in mild reaction conditions and recycling of recovered catalyst are notable green features and advantagesof this method[5].

Kan Nie, M.A(2001) investigated the Friedel-Craftsalkylation reaction of triphenylmethanol with methoxybenzene (anisole) in supercritical and subcritical carbon dioxide, and undersolventless reaction conditions. The reaction was initiated using trifluoroacetic acid to produce Triphenylmethylcarbocation as the reaction intermediate. Isolated product yields of the Friedel-Crafts product, p-methoxytetraphenylmethane[6].

Agee B M., et al., (2013) carried out the synthesis of isobutyrophenone through a Friedel–Crafts acylation of benzene, using the solar reflector. A 66% yield (9.70 g) of isobutyrophenone was obtained when the Friedel–Crafts acylation of benzene was performed with the solar reflector during the summer of 2012, while the comparative study using an electric heat source only had a 44% yield (6.73 g) of isobutyrophenone. The in-lab synthesis of isobutyrophenone reported is for one single experiment. Multiple attempts of synthesizing isobutyrophenone in-labwere performed and resulted. Furthermore, the solar reflector was able to produce a purer product based off of the NMR spectra of the product[7].

The reaction of an acid chloride with an aromatic substrate requires a greater than stoichiometric quantity of Aluminium chloride which acts as the "catalyst" (>2 mole equivalents in sulfonylations). Every molecule of the ketone product produces a complex with one molecule of the catalyst, effectively removing it from the reaction. By using a water quench, the organic product is releasedwith the resulting emission of about 3 equivalents of HCI, which need to be scrubbed from

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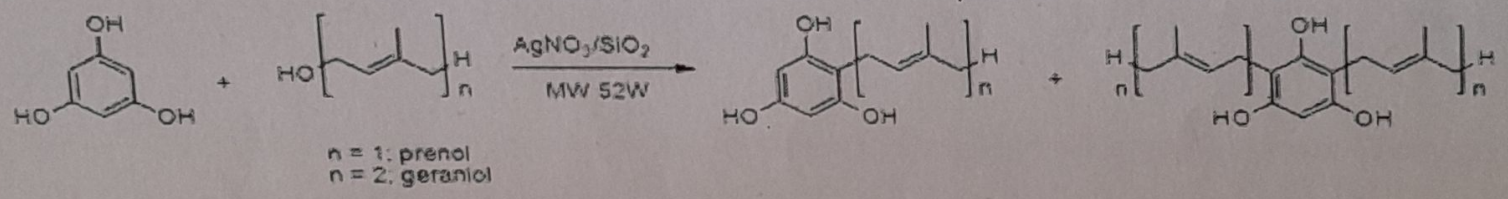
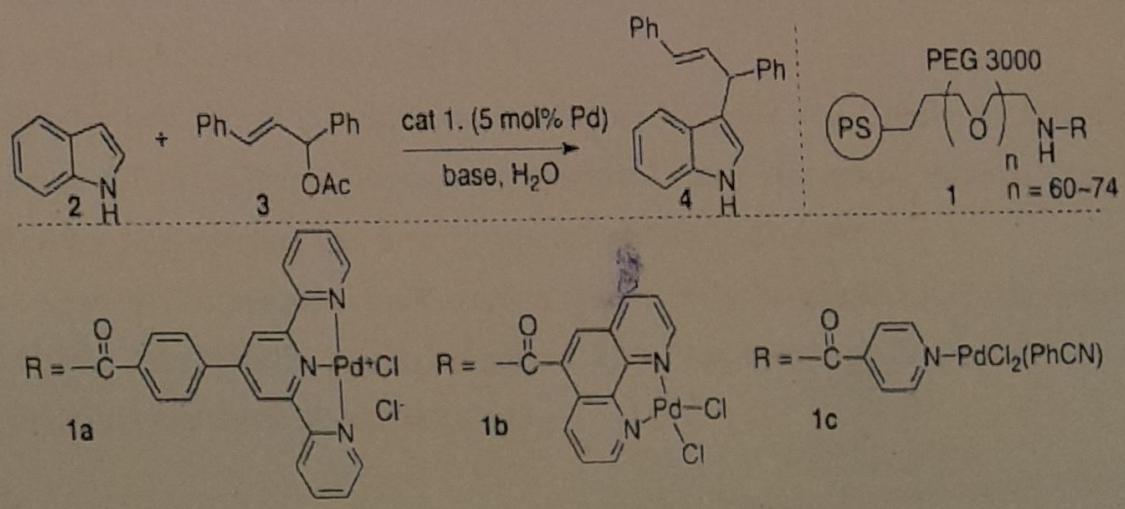
the off gases and leads to the production of 3 equivalents of salt waste. As soon as the organic product has been recovered, aluminous water remains, which must also be disposed. The overall process generates more waste than product[8].

Alejandra P.et al (2015) developed a new rapid and efficient method for the synthesis of a series of alkylated phloroglucinols using conventional microwave is reported 4 phloroglucinol derivatives (4, 5, 6 and 7) were synthesized with good yields (~50%) by a Friedel-Crafts reaction through an Electrophilic Aromatic Substitution mechanism between geraniol/prenol and phloroglucinol, using reusable SiO2 and AgNO3 as the best catalyst tested without solvents under microwave irradiation. They used silica gel that facilitates the provision of phloroglucinol during the reaction. Using AgNO3, a less toxic catalyst instead of the commonly used BF3, AlCl3, SnCl4, AuCl3. Their methodology produced higher amounts (grams) in a short time without using solvents[9].



Aribert, et al (2010) carried out conventional organic solvent (1-2 dichlorobenzene),zeolite Y proved to be the more appropriate solid catalyst for the FriedelCrafts acylation of a benzofurane derivative by an acid chloride. The differentexperiments carried out with zeolite Y (15) have given promising results, wherefew by-products were generated[10].

SuzukaT et al (2020) carried out Friedel-Crafts-type alkylation of indoles with allylic ester using the PS-PEG resin-supported phenanthroline-palladium complex to give the 3-allyl-1H-indoles with up to 91% yield. This polymeric catalyst was also found to promote the C3-alkylation reaction to give a thermodynamic alkylation product with high selectivity. This catalyst was recovered and reused several times without any loss of activity[11].



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II CONCLUSION

During the last two decades Fiedel-Crafts reaction has undergone a tremendouschange. It is observed that toxic catalyst has been slowly replaced in recent works not only in terms of new methodologies but also in the development of new catalyst, strategies, new reagents involving green concepts of atom economy and selectivity.

REFERENCES

1. Friedel and J. M. Crafts , Compt. Rend., 1877, 84 , 1392 —1395
2. M. Rueping and B. J. Nachtsheim ,Beilstein J. Org. Chem., 2010, 6 , 1 —31 Search PubMed .
3. M. B.Smith and J.March, March's advanced organic chemistry: reactions, mechanisms, and structure, John Wiley & Sons, 2007.
4. Majid M. Heravi, Orcidlogo ,VahidehZadsirjan, PegahSaedia and TayebehMomenia;Applications of Friedel–Crafts reactions in total synthesis of natural products RSC Adv., 2018,8, 40061-40163
5. Kartik Kumar Nandi Sustainable catalyst for friedel–crafts acylation,Catalysis in Green Chemistry and Engineering, 1(2):149–153 (2018)
6. Kan Nie; An investigation of friedel-crafts alkylation reactions insuper- and subcritical carbon dioxide and under sol ventless reaction conditions(thesis)Western Michigan University Kalamazoo, MichiganApril 2001
7. Brian M. Agee, Gene Mullins, and Daniel J. Swartling;Friedel–Crafts Acylation Using Solar Irradiationdx.doi.org/10.1021/sc4002802 | ACS Sustainable Chem. Eng. 2013, 1, 1580–1583
8. Furniss, B. S.; Hannaford, A. J.; Smith, P. W. G.; Tatchell, A. R.Vogels Text Book of Practical Organic Chemistry, 5th ed.; Longman:Singapore, 1989; Kirk-Othmer, Encyclopedia of Chemical Technology,5th ed.; 1997; Vol. 24, p 38.
9. Alejandra P. Vergara,Javier A. ContreraS, Mauricio E. Osorio and Marcela A. Carvajal J;Rapid method of friedel-crafts alkylation of phloroglucinol by microwave in dry media and reusable catalyst. Chil. Chem. Soc. vol.60 no.3 2015
10. Aribert, Nicolas and Camy ,Séverine and Lucchese,Yolande and Condoret, Jean-Stéphane and Cognet, Patrick (2010) Cleaner Routes for Friedel-Crafts Acylation. International Journal of Chemical Reactor Engineering, vol. 8 (n°1). pp. A53 ISSN 1542-6580
11. Toshimasa Suzuka*,YutoOoshiroandKazuhitoOgihara ;Friedel–Crafts-Type Alkylation of Indoles in Water Using Amphiphilic Resin-Supported 1,10-Phenanthroline–Palladium Complex under Aerobic Conditions;Catalysts 2020, 10(2), 193;

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