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# An Efficient Acetylation of Aromatic Hetero Cyclic Compounds: Silica Gel As Well As Silica-Ferric Oxide Supported Erbium (III) Triflate Used As A Novel Catalyst For First Time Under Solvent Free Conditions

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## ABSTRACT

2-acylated aromatic five membered heterocyclic compounds are selectively synthesized using Silica-Erbium (III) Triflate and Silica-Ferric oxide-Erbium (III) Triflate as new catalytic systems as much as prominent acylating agents at varying temperature conditions. The most common oxidation sates of the Erbium $^{+3}$ and Fe $^{+3}$ are support to bind the anions to high activation due to the solidified addition of silica gel, silica-ferric oxide as other hand for the catalytic reaction and to give excellent quantity, quality of product in terms of yields. The easy and safe handling of the high reactive erbium triflate loaded on the silica gel reduces the reaction time (1-1.5 hrs) hours, thermal conditions (20$^0$C-45$^0$C) and without using solvent media to obtain better yields of 2-acylated aromatic heterocyclic molecules. The plausible mechanism of Friedel crafts acylation has been suggested.

**Keywords:** Silica gel, Erbium (III) triflate, Ferric oxide, Lewis acid catalyst, acylation, selectivity

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## INTRODUCTION

Lanthanoid family is found to possess varying promising catalytic activities. Many examples exist where rare-earth metals are used as Lewis acid catalysts with efficacy varying from one reaction to another [1-7]. Many of these reagents are highly corrosive and difficult to handle, while some Lewis acid catalysts are rather expensive and moisture sensitive. The present day research has been focused on the benign, green reactions in organic chemistry, of which one among them is solid support synthesis. Er (III) compounds are highly efficient catalysts[8] for several important reactions such as Diels alder cycloaddition[9], acylation[10], formation of t-butyl ethers[11], synthesis of imines[12], acetonides[13-17]. To overcome the moisture sensitivity of these erbium catalysts, we have developed a new method for the usage of Erbium triflate and enhancement of $sp^2$ hybridized CH-activation by providing the large surface area. First time reported the novel application of $SiO_2$-Erbium (III) Triflate and $SiO_2$-$Fe_2O_3$-erbium (III) triflate as efficient catalyst systems in selective acylation of aromatic five membered heterocyclic compounds.

2-acetylated thiophene, pyrrole and furan are the most versatile and prime precursors in the synthetic organic chemistry. Many procedures or methods are reported for the acylation of aromatic heterocyclic compounds. The 3-acyl hetero aromatic compound is the usual contaminate present to the extent of 20-25 % in the acylation process by directly using soluble acids. The use of excess reagent acetic anhydride and 3-acetyl heterocyclic molecule, the by-product are the major disadvantages for the quality of end products. As a part of continued research interest in development of novel catalyst systems, the catalytic activities of silica supported Erbium (III) triflate doping with and without $Fe_2O_3$ in the preparation of 2-acylated thiophene, pyrrole and furan in terms of conversion and selectivity have been studied and the results are the subject of this paper .We reporting here that we had succeeded to reduce the time intervals, thermal conditions from $20^0$ C to $45^0$ C Which was almost just above the room temperature for the sake of handling and much easier to get product. No use of solvent to obtain the products [18-20].

## EXPERIMENTAL

### Preparations of catalysts:

### Catalytic system-A:

Er (III)-Triflate-$SiO_2$ (silica gel-GF-254), purchased from fluka chemicals were used as such. To a 50 gm of $SiO_2$ add 25gm of Er (III) Triflate in a dried round bottom flask and grained until material becomes the amorphous powder under nitrogen atmosphere.

### Catalytic system-B:

Er (III)-Triflate-$SiO_2$ (silica gel-GF-254), purchased from fluka chemicals were used as such. To a 50 gm of $SiO_2$ add 25gm of Er (III) Triflate in a dried round bottom flask and grained until material becomes the amorphous powder and later add 13 gm of $Fe_2O_3$ (Ferric oxide) under nitrogen atmosphere.

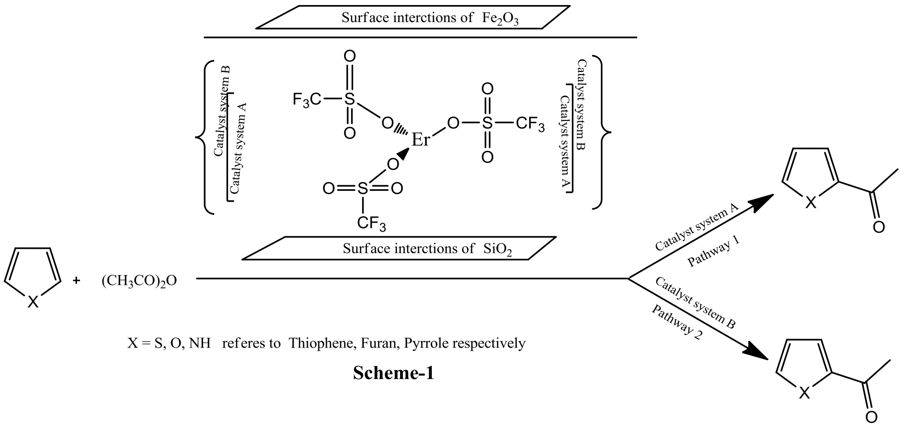
**Typical procedure for the Friedel Craft's acylation:**

Add a Catalyst system-A $SiO_2$-Erbium (III) Triflate (0.3mg) to the solution of aromatic heterocycle (3.5 mmol) and acylating agent (5.5 mmol) under nitrogen atmosphere. The mixture was stirred for the given time at various temperatures from 20-45$^0$C. The reaction mixture turned to light green. The reaction was monitored by GC chromatograph at several interval times (GC17A-Gaschromatograph Shimdazu). The maximum conversion of product was reached from 1hr to 1.5 hrs only. After the completion of the reaction, the crude product was treated with the 10ml of sodium bicarbonate (5%) solution and was extracted with the dichloromethane (2 x 10 ml).The organic layer was separated out and treated with the anhydrous crystals of magnesium sulfate (4 gm) to remove the water droplets and salts for several times. Finally the solvent and product was distilled out with high vacuum. On the other hand the same procedure had repeated with the catalyst system-B as $SiO_2$-$Fe_2O_3$-erbium (III) triflate.

**$^1$HNMR DATA**

2-acetyl thiophene: δ = 2.4 (3H, s), δ = 7.8 (1H, dd), δ = 7.7 (1H, d), δ =7.4 (1H, d) 2-acetyl furan: δ = 2.58 (3H, s), δ = 7.0 (1H, dd), δ = 7.25 (1H, d) δ = 7.8 (1H, d). 2-acetyl pyrrole: δ = 2.5 (3H, s), δ = 6.7 (1H, dd), δ 6.8 (1H, m), δ =7.3 (1H, d), δ = 9.8 (1H, brs)

The five membered aromatic heterocycle and acetic anhydride were reacted in the presence of $SiO_2$-Erbium (III) Triflate, $SiO_2$-$Fe_2O_3$-erbium (III) triflate to obtain the corresponding product of 2-acylated pyrrole, thiophene, and furan respectively at the average of 90% yields as shown in the table 1. The reactions were completed within 2 to 2$^1$/$_2$ hours under the nitrogen atmosphere at various temperaures. A comparative study was carried out for this electrophillic substitution reaction while using the catalyst erbiumtriflate supported by silica gel and ferric oxides in minimum quantities respectively and individual combinations.



**Scheme-1**

**Table 1**

| S.No | Aromatic heterocycle | Catalyst | Temp ($^0C$) | Time (Min) | Conversion [a] | Selectivity [b] |
|---|---|---|---|---|---|---|
| 1 | Thiophene | A | 20 | 15 | 35 | 50 |
| 2 | Thiophene | A | 25 | 30 | 40 | 57 |
| 3 | Thiophene | A | 30 | 45 | 60 | 69 |
| 4 | Thiophene | A | 35 | 60 | 68 | 76 |
| 5 | Thiophene | A | 40 | 75 | 77 | 82 |
| 6 | Thiophene | A | 45 | 90 | 88 | 93 |
| 7 | Furan | A | 20 | 15 | 50 | 40 |
| 8 | Furan | A | 25 | 30 | 56 | 49 |
| 9 | Furan | A | 30 | 45 | 63 | 62 |
| 10 | Furan | A | 35 | 60 | 70 | 70 |
| 11 | Furan | A | 40 | 75 | 80 | 84 |
| 12 | Furan | A | 45 | 90 | 82 | 91 |
| 13 | Pyrrole | A | 20 | 15 | 45 | 50 |
| 14 | Pyrrole | A | 25 | 30 | 67 | 63 |
| 15 | Pyrrole | A | 30 | 45 | 75 | 72 |
| 16 | Pyrrole | A | 35 | 60 | 78 | 80 |
| 17 | Pyrrole | A | 40 | 75 | 84 | 87 |
| 18 | Pyrrole | A | 45 | 90 | 90 | 90 |
| 19 | Thiophene | B | 20 | 15 | 51 | 61 |
| 20 | Thiophene | B | 25 | 30 | 59 | 71 |
| 21 | Thiophene | B | 30 | 45 | 67 | 79 |
| 22 | Thiophene | B | 35 | 60 | 75 | 85 |
| 23 | Thiophene | B | 40 | 75 | 81 | 89 |
| 24 | Thiophene | B | 45 | 90 | 89 | 99 |
| 25 | Furan | B | 20 | 15 | 39 | 58 |
| 26 | Furan | B | 25 | 30 | 48 | 68 |
| 27 | Furan | B | 30 | 45 | 60 | 79 |
| 28 | Furan | B | 35 | 60 | 71 | 86 |
| 29 | Furan | B | 40 | 75 | 79 | 89 |
| 30 | Furan | B | 45 | 90 | 85 | 98 |
| 31 | Pyrrole | B | 20 | 15 | 53 | 60 |
| 32 | Pyrrole | B | 25 | 30 | 59 | 70 |
| 33 | Pyrrole | B | 30 | 45 | 67 | 79 |
| 34 | Pyrrole | B | 35 | 60 | 74 | 85 |
| 35 | Pyrrole | B | 40 | 75 | 80 | 88 |
| 36 | Pyrrole | B | 45 | 90 | 85 | 98 |

[a] GC monitoring, [b] Products conformed by proton NMR.

## RESULTS AND DISCUSSIONS

The present catalyst system has been highly effective and convenient for the acetylation of aromatic hetero cycles to afford the good products. Both the catalyst systems for the acetylation of aromatic heterocyclic substrates are shown in the scheme 1 as and has separately subdivided as two path ways {path way-1(Catalyst System-A)} and {path way-2(Catalyst System-B)}.The results on catalytic activity, selectivity of various catalysts in the acylating of hetero aromatic compounds with acetic anhydride conducted are represented in table 1. Encouraged by the results obtained with thiophene, we had continued and applied this methodology to a different aromatic five membered heterocyclic substrates such as pyrrole, furan under same reaction conditions. We had not been found the byproducts like 3-acylated substitutions, where as this was a very common challenge in Friedel-Craft's acetylation reactions. The methodology is proved to be general and could be applied to a broad range of five membered hetero aromatic molecules. Interestingly, the acylations in the presence of Er (III)-Triflate-silicagel-ferricoxide catalyst showed more efficacies. We had not attempted to use any organic solvents in this reaction due to the previous research experience of my report [21]. The anxiety to find new catalysts in the field of acyaltion reactions in organic chemistry, we had tried this catalytic system for the for the first time by improving the surface of the catalyst using the silica gel, ferric oxide. The catalyst activity increased with the degree of exchange of $Er^{3+}$ ions by $Fe^{3+}$ ions. Plotting the conversion, selectivity, time factors we had concluded the reactions are pseudo first order from the slopes of straight lines.

After the completion of the reaction, we had recovered the erbium (+3) (78%, pale colour), Fe (+3) (80%, light brown colour) with the amorphous powder of silica gel respectively by the evoparation of aqueous phases under reduced pressure in the work up. These recovered catalysts were reused for four times by drying over the $P_2O_5$.

In summary, it would appear that the combination of a these catalyst systems and acetic anhydride is a simple and practical method for the selective 2-acylation of aromatic five membered molecules.

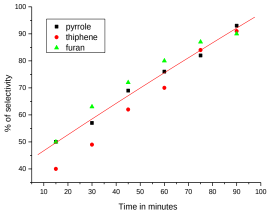


**Fig.1: plot of –ln(1-X) of acylated aromatic heterocycle vs. time (minutes). Catalyst system-A $SiO_2$-Erbium (III) Triflate (0.3mg) to the solution of aromatic heterocycle (3.5 mmol) and acylating agent (5.5 mmol) under nitrogen atmosphere**

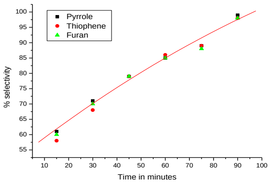


**Fig.2: Plot of –ln (1-X) of acylated aromatic heterocycle vs.Time (minutes). Catalyst system-A $SiO_2$-Erbium (III) Triflate (0.3mg) to the solution of aromatic heterocycle (3.5 mmol) and acylating agent (5.5 mmol) under nitrogen atmosphere**

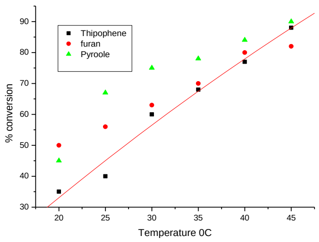


**Fig.3: Plot of –ln (1-X) of acylated aromatic heterocycle vs.temperature. Catalyst system- $SiO_2$-$Fe_2O_3$-erbium (III) triflate (0.3mg) to the solution of aromatic heterocycle (3.5 mmol) and acylating agent (5.5 mmol) under nitrogen atmosphere**

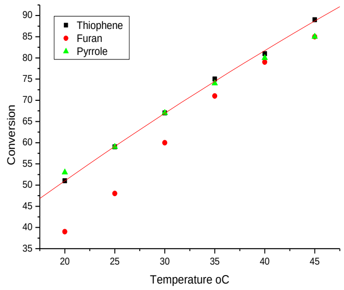


**Fig.4: Plot of –ln (1-X) of acylated aromatic heterocycle vs. temperature. Catalyst system-B $SiO_2$-Erbium (III) Triflate (0.3mg) to the solution of aromatic heterocycle (3.5 mmol) and acylating agent (5.5 mmol) under nitrogen atmosphere**

## CONCLUSIONS

In conclusion, this methodology provides the tangible catalytic activity of ecofriendly catalysts Er (III)-Triflate-silica gel and for the preparation of the 2-acylated aromatic heterocyclic intermediates by acylating aromatic heterocyclic compounds with acetic anhydride at various time intervals, thermal conditions. Which catalysts are more prominent in the handling of the chemicals in at bench work. Erbium triflate is the one of the cheapest catalyst. Without significant loss of catalytic activity, the catalysts can be reused four times after the reaction completion .The usage of low percentage of catalyst can be given the good results and yields. Reactions can run in safe modes and conditions.

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