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Research Article

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Utility of periodic mesoporous silica chloride (PMSi-Cl) for the synthesis of quinolines compounds in different name reactions

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ABSTRACT

Silica chloride serves as an efficient solid acid catalyst in different named reactions such as; 1. Combes Synthesis 2. Knorr Synthesis 3. Doeber von-Miller Synthesis 4. Skrup's Synthesis for the synthesis of quinoline compounds. The yields are excellent and the procedure is simple and convenient, with the higher catalytic efficiency of a heterogeneous system.

Keywords: Silica chloride, quinoline, Combes, Knorr, Doeber Miller, Skrup's Synthesis

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INTRODUCTION

The development of environmentally benign technologies is the most challenging goal of contemporary chemistry and chemical engineering. Environmentally friendly chemical processes should be designed to use ecologically benign feeds and solvents, and utilize efficient systems that recycle reagents and catalysts. In the development of industrial processes, efficient separation of reagents and catalysts to enable their reuse for subsequent reaction cycles is a key challenge, and has been increasingly appreciated, especially in the stream of green chemistry [1].

In addition, current research and general interest in heterogeneous systems is also increasing due to the higher catalytic efficiency such systems possess to meet the needs of industry and developing technologies [2]. Solid supports have found wide applications in organic reactions [3]. They mostly facilitate the work-up of the reaction, and high selectivity accompanied with high yields of the products are usually observed. Silica gel is used extensively as a support in organic chemistry [4].

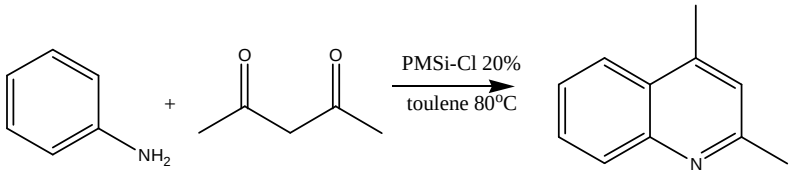
Modified silica supports for functional-group transformation are also of interest. Silica chloride can be easily prepared from the readily available materials, silica gel and thionyl chloride [5]. Furthermore, silica chloride does not dissolve in organic solvents, and so can easily be removed from the reaction mixture and reused. The only by-product of the reaction is water; thus, there is no problem relating to the removal of side products, and the experimental procedure itself is very simple[6]. Present work we intended to describe the utility of silica chloride in Combes Quinoline Synthesis, Knorr Quinoline Synthesis, Doebner-von Miller Synthsis and Skrup's Synthesis. All these synthesis reactions lead to the formation of quinoline derivatives by simple greener method by carbon-carbon bond formation.

EXPERIMENTAL SECTION

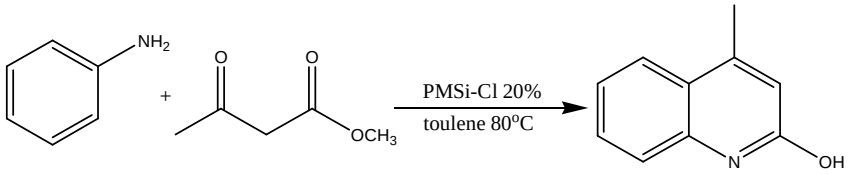
2.1 *Materials, methods and instruments***:**
Melting points were determined in open capillaries and are uncorrected. IR (KBr) spectra were recorded on Perkin Elmer-577 spectrophotometer, NMR spectra on Varian Mercury YH-300 spectrometer with TMS as internal standard using $CDCl_3$ and DMSO as solvent. Purity of the compounds was checked by TLC.

2.2 *Periodic Mesoporous Silica Chloride (PMSi-Cl)*
To well-stirred silica gel (20 g) in CH_2Cl_2 (50 mL) was added dropwise $SOCl_2$ (20 g) at room temperature. Evolution of copious amounts of HCl and SO_2 occurred instantaneously. After stirring for 1 h, the solvent was removed to dryness under reduced pressure (1 Torr). The SiO_2–Cl could be stored in sealed vessels for 6 months without any critical decline in activity.

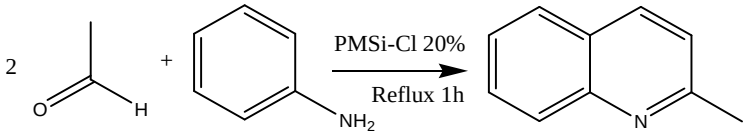
2.3 *Preparation of Quinoline:*
2.3(a) By Combes Quinoline Synthesis:
pentane-2,4-dione (1 mmol) and aniline (1 mmol) were mixed with periodic mesoporous silica chloride 20% and heated at 80^{o}C in toulene for one hours. After completion of the reaction as indicated by TLC (hexane/ethyl acetate 8:2), the reaction mixture was brought to room temperature. Reaction mixture was washed by cold water and then filtered. The filtrate was concentrated and the solid product was recrystallized from ethanol to give the pure product.



2.3(b) By Knorr Quinoline Synthesis:
Methyl acetoacetate (1 mmol) and aniline (1 mmol) were mixed with periodic mesoporous silica chloride 20% and heated at 80^{o}C in toulene for one hours. After completion of the reaction as indicated by TLC (hexane/ethyl acetate 8:2), the reaction mixture was brought to room temperature. Reaction mixture was washed by cold water and then filtered. The filtrate was concentrated and the solid product was recrystallized from ethanol to give the pure product.

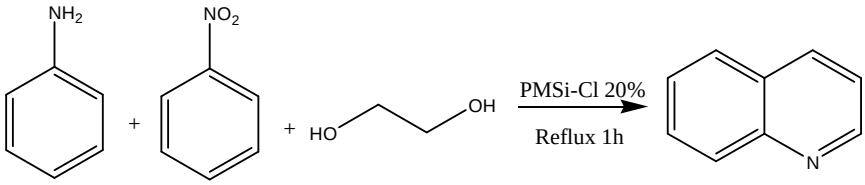


2.3(c) By Doebner-von Miller Synthesis:
Formaldehyde (1 mmol) and aniline (1 mmol) were mixed with periodic mesoporous silica chloride 20% and refluxed one hour. After completion of the reaction as indicated by TLC (hexane/ethyl acetate 8:2), the reaction mixture was brought to room temperature. Reaction mixture was washed by cold water and then filtered. The filtrate was concentrated and the solid product was recrystallized from $CHCl_3$ to give the pure product.



2.3(d) By Skrup's Synthesis:
Ethylene glycol (1 mmol), aniline (1 mmol) and nitrobenzene (1.5 mmol) were mixed with periodic mesoporous silica chloride 20% and heated at 80^{o}C in toulene for one hours. After completion of the reaction as indicated by TLC (hexane/ethyl acetate 8:2), the reaction mixture was brought to room temperature. Reaction mixture was

washed by cold water and then filtered. The filtrate was concentrated and the solid product was recrystallized from ethanol to give the pure product.



RESULTS AND DISCUSSION

Silica chloride is one of the most versatile and utilized catalyst for the selective construction of heterocyclic ring systems, in particular for the synthesis of quinolines. This new synthetic strategy resulted in a remarkable improvement in synthetic efficiency, and more importantly, it enhanced the utilization efficiency of the modified silica chloride, decreases the production of chemical waste without using highly toxic reagent for the synthesis of quinoline derivatives.

The Si-Cl bond is labile and can give rise to Lewis acid centers on silica. The Cl is easily displaced selectively by a nucleophilic substitution reaction generating a cationic centre on the carbonyl carbon which is easily attacked by the nucleophile.

The physical characterization data of the compounds synthesized are given in the following table.

Sr. No.	Compounds	Structure	Molecular formula	Percentage yield	Melting point
1.	2,4-dimethylquinoline	A	$C_{11}H_{11}N$	62.19%	281°C
2.	4-methylquinolin-2-ol	B	$C_{10}H_9NO$	57.11%	337 °C
3.	2-methylquinoline	C	C10H9N	59.44%	241°C
4.	quinoline	D	C_9H_7N	61.17%	228°C

CONCLUSION

In summary, we have described an improved procedure for Combes Synthesis, Knorr Synthesis, Doeber von-Miller Synthesis, Skrup's Synthesis the reaction. The use of silica chloride as heterogeneous catalyst has made this method very cost effective. Another advantage of this method is excellent yields in shorter reaction time with high purity of the products.

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