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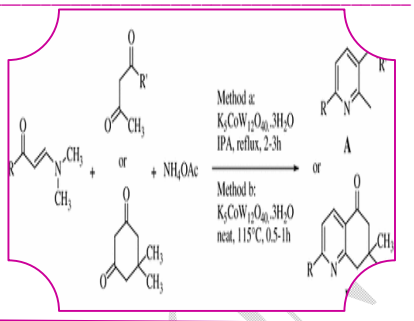
SYNTHESIS OF QUINOLINE DERIVATIVES AND ITS APPLICATIONS TO SOME REACTIONS BY SUPPORTED HETEROPOLY ACIDS (HPAS)



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ABSTRACT

Diverse types of heteropoly acids (HPAs) and supported ones on solids with different nature and textural properties were used in some reactions in order to obtain quinoline derivatives. This conversion has been preceded by tungsto-phosphoric acid supported on silica, KSF and activated carbon as optimized catalysts in high yields and short reaction times. The general applicability of this method is demonstrated by using various substrates including ketones, ketoesters and diketones. These catalysts were found to be reusable and considerable catalytic activity could still be achieved after the runs.

KEYWORDS: *Quinoline derivatives, solvent-free condition, supported catalysts, heteropoly compound.*

1. INTRODUCTION:

Several N-heterocyclic compounds are vulnerable to microbial deprivation. They frequently stay alive in biologically vigorous natural yields and synthetic compounds of medicinal awareness. Various quinoline derivatives have the prospective of both inhibiting PrPres formation and delaying the incubation phase of germ-infested animals.

A variety of bioactive compounds such as antibacterial, anti-inflammatory, antiasthmatic etc. restraining mediator have a quinoline ring in their structures have the medicinal applications employed in the study of bio-organic and bio-organo-metallic practices and also in the creation of polymers that intermingle improved electronic, mechanical and allied properties.

Different protocols have been developed for the synthesis of quinoline derivatives such as Friedlander annulations which is one of the most effortless looms for the synthesis of poly-substituted quinolines.

These reactions are usually conceded in existence of a base or by heating a blend of the reactants at elevated temperatures in the dearth of catalyst. In current times, quite a lot of Brönsted and Lewis acids have been utilized for this conversion. The majority of the synthetic methods endure from the inconveniences for instance small capitulate of products, prolonged reaction times, insensitive reaction conditions etc.

To facilitate or surmount these restrictions, the development of a simple, efficient, and high-yielding protocol, with short reaction time is still enviable. Heteropoly acids, HPAs, and their salts, are commonly used as catalysts in homogeneous and heterogeneous systems due to their high stability, availability, and strong acidity and redox properties.

These compounds have been extensively investigated with respect to their properties and applications. Beside various advantages of HPAs, the disadvantage of these catalysts is that their specific surface area is very low (Of the order of less than 10 m^2 /g).

So as to augment specific surface area, various supports have been exercised for diffusion of HPAs on a high surface area. Restriction of HPAs on supports leads to increased surface area, increased active site accessibility, and higher dispersion of acidic protons.

In this work, we have explored the catalytic recitation of commodity available HPAs on different carriers in the condensation reaction of 2-aminoacetophenone and a variety of carbonyl compounds by way of Friedlander reaction.

2. EXPERIMENTAL:

2.1. Chemicals Procured

S.N.	CHEMICAL	MFG. COMPANY	PURITY
1	$H_3PW_{12}O_{40}$ (Q_1)	Aldrich	99%
2	$H_3PMo_{12}O_{40}$ (Q_2)	Aldrich	99%
3	$H_4SiW_{12}O_{40}$) (Q_3)	Aldrich	99%
4	Hydrate and γ-Alumina	Aldrich	99%
5	Activated Carbon	Merck	99%
6	KSF	Merck	99%
7	K_{10} Montmorillonite	Merck	99%
8	Silica	Merck	99%
9	Titania	sd fine	99%

Products were characterized by comparing their spectral data with those of genuine samples.1H NMR spectra were recorded on a BA0.2 GHz NMR spectrometer with $CdCl_3$ as the solvent and TMS as the internal reference. C-H-N compositions were measured by EDAX model Euro EA3000.

2.2. Preparation of Supported Catalysts

Supported Q_1 catalysts were prepared by the dripping impregnation technique. Silica-supported Q_1 catalysts were prepared by impregnating silica (25mg) with an aqueous solution of Q_1 (16mg in 20mL water).

The blend was stirred overnight at RT, followed by drying using a rotating evaporator. For preparation of the K_{10}-supported Q_1 catalyst, K_{10} Montmorillonite was dried in an oven at 373K for 120min prior to its use as a support. After drying, 40mg of K_{10} was taken.

To prepare a catalyst with 40 % loading of Q_1, 16mg of Q_1 was dissolved in 3mL of dry methanol. This solution was added bit by bit to pre-dried K_{10} with constant stirring using a glass rod.

Primarily, with addition of Q_1 solution, the clay was in a powdery form, but on further addition of Q_1 solution, the clay turned into a paste which on further stirring for 10 min, resulted in a free flowing powder.

A similar procedure was followed for the synthesis of KSF-supported Q_1 catalyst. A catalyst based on Q_1 supported on γ-Al_2O_3 was also prepared. The solution of Q_1 was prepared by dissolving 16m Q_1 in each 20mLof water and methanol. Then 40mg γ-Al_2O_3 was dropped into the above solution under vital stirring for a day.

For the preparation of carbon-supported Q_1 catalyst, carbon was first subjected to an acid and base treatment to remove impurities. This catalyst was prepared by the pore filling impregnation technique with a Q_1 solution. After the impregnation, the catalyst was dried at room temperature for a day, and calcined at 473K for 180min.

All catalysts were characterized and identified by comparing their spectral and analytical data with those of standerd samples.

2.3. Synthesis of Compounds

A fusion of 1.0 mmol of 2-aminoacetophenone, 1.2 mmol of substrates, and a suitable quantity of catalyst, were crushed at 373K under solvent-free condition. After completion of the reaction, as indicated by TLC, the reaction mixture was diluted with 4.5mL of CH_3CN and filtered.

The catalyst was recovered from the filtrate. The filtrate was concentrated and the product was purified by column chromatography on silica gel using EtOAc/hexane as efluent. All products were identified by comparing of their spectral data with those of genuine samples. The recovered catalyst was washed with 300 mL of ether and reused.

Scheme 1: From the reaction of 2-aminoacetophenone with ethyl acetoacetate then 89–93% of ethyl-2,4-dimethylquinoline-3-carboxylate was obtained as a smear with oil.

Scheme 2: From the reaction of 2-aminoacetophenone with methyl acetoacetate then 88–91% of methyl-2,4-dimethylquinoline-3-carboxylate was obtained as smear with oil.

Scheme 1: δH (200 MHz, $CDCl_3$): 1.40 (3H, t, *J* 7.1 Hz, CH_3), 2.57 (3H, s,CH_3), 2.68 (3H, s,CH_3), 4.42 (2H, q, *J* 7.1 Hz,OCH_2), 7.46–7.51 (1H, m, CH), 7.62–7.65 (1H, m, CH),. 7.91 (1H, d, *J* 8.0 Hz, CH), 7.98 (1H, d, *J* 8.0 Hz, C-CH); δc (200 MHz, $CDCl_3$): 14.0, 19.8, 22.4, 60.7, 124.0, 125.3, 126.0, 128.1, 131.1, 144.7, 147.9, 158.6, 165.5; HRMs found: M, 229.272; Calc. for C14H15NO2: 229.274; (Found: C, 73.45; H, 6.57; N, 6.04 %. Calc. for $C_{14}H_{15}NO_2$ (229.27); C, 73.34; H, 6.59; N, 6.11 %).

Scheme 2: δH (200 MHz, $CDCl_3$): 2.58 (3H, s, CH_3), 2.70 (3H, s, CH_3), 3.96 (3H, s, OCH_3), 7.01–7.06 (1H,m, CH), 7.68–7.72 (1H,m, CH), 7.96 (1H, d, *J* 8.0 Hz, C-CH), 8.01 (1H, d, *J* 8.0 Hz, C-CH); δc (200 MHz, $CDCl_3$): 19.9, 22.5, 51.1, 123.9, 124.8, 126.0, 128.1, 131.8, 145.4, 148.8, 158.2, 166.1;HRMsfound: M, 215.246; Calc. for $C_{13}H_{13}NO_2$: 215.248; (Found: C, 72.61;H, 6.06; N, 6.47 %. Calc. for $C_{13}H_{13}NO_2$ (215.25); C, 72.54; H, 6.09; N, 6.51 %).

The reaction of 2-aminoacetophenone and ethyl acetoacetate as model reactants was studied in the presence of 0.2 g of Q_1 catalyst under solvent-free condition at different temperatures. In the presence of this catalyst, desired product was observed at elevated temperature after 1 h. The yield of product is extensively increased to 90% after 60 minutes. In the presence of 0.2 g of other HPAs including Q_2 and Q_3, quinoline product was obtained in lower yields in comparison with Q_1.

4. CONCLUSION:

In this article we have described a rapid, efficient, environmentally and economically benign method for the synthesis of quinoline derivatives by the Friedlander condensation under solvent-free conditions in the presence of low amounts of Q_1/SiO2, Q_1/KSF and Q_1/C with the excellent yields.

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