Silica sulfuric acid (SSA) a novel catalyst for synthesis of some α-phenylhydrazone-2-ketomethylquinolines

Amir Landarani-Isfahani1,2*, Javad Safari2*, Marziyeh Ghotbinejad2, Soheyla Gandomi-Ravandi2, Moshtael2
1Department of Chemistry, University of Isfahan, Isfahan-81746-73441, (IRAN)
2Department of Chemistry, Faculty of Sciences, University of Kashan, Kashan 87317-51167, (IRAN)
E-mail : Landarani@sci.ui.ac.ir
Received: 11th December, 2008 ; Accepted: 16th December, 2008

ABSTRACT
Silica sulfuric acid as an efficient and reusable heterogeneous catalyst have been used for the preparation of α-phenylhydrazone-2-ketomethylquinoline derivatives from 2-ketomethylquinoline and aniline derivatives by mild and solvent-free conditions in good to excellent yields and short reaction times.
© 2009 Trade Science Inc. - INDIA

1. INTRODUCTION
Acidic catalysts have been used, mainly in industry, for producing more than $1 \times 10^8$ Mt/year of products[1]. Among acidic catalysts, the most commonly used are HF, H$_2$SO$_4$, HClO$_4$, and H$_3$PO$_4$ (in liquid form or supported on Kieselguhr). Solid acids have many advantages such as ease of handling, decreasing reactor and plant corrosion problems, and environmentally safe disposal[1,2]. Also, wastes and by-products can be minimized or avoided by developing cleaner synthesis routes[3]. Green chemistry has been defined as a set of principles that reduce or eliminate the use or generation of hazardous substances. In addition, there is current research and general interest in heterogeneous systems because of their importance in industry and in developing technologies[4]. Heterogeneous organic reactions have proven useful to chemists in the laboratory as well as in the industrial context. These reactions are effected by the reagents immobilized on the porous solid supports and have advantages over the conventional solution phase reactions because of the good dispersion of active reagent sites, associated selectivity and easier work-up[5].

In recent decades, organic color chemistry is undergoing very exciting development as a result of the opportunities presented by dye applications in high technology fields: electronic devices, linear and nonlinear optics, reprography, sensors, and biomedical uses[6]. Numerous methods are available for the reduction of arenediazonium salts[7]. The reactions of arenediazonium salts with various carbon nucleophiles such as Grignard reagents, enamines, enolether, lithium enolates of ketones or esters, and ketene silyl acetals[8] lead to the formation of azo or hydrazo compounds. Azo dyes are the largest and most versatile class of dyes[9,10]. Aliphatic azo compounds in which the carbon containing the azo group is attached to hydrazones that are the products of the reaction. Nevertheless the development of new synthetic methods for the efficient preparation of azo dyes containing aromatic ring fragment is therefore an interesting challenge. In last paper, We reported α-phenylhydrazone-2-ketomethylquinoline by homogenous methods[11,12] and our data shown hydrazone forms

KEYWORDS
Silica sulfuric acid; Heterogeneous catalyst; Solvent free; Aryldiazonium ion; 2-Ketomethylquinolines.
whereas this paper suggests special silica sulfuric acid (SSA) as novel catalyst for preparation of aryldiazonium ions and azo couple reaction. Silica sulfuric acid is safe, easy to handle, environmentally benign with fewer disposals problems that was prepared from the reaction of silica gel with chlorosulfonic acid[13].

2. EXPERIMENTAL

2.1. Instrumentals and materials

All reagents were purchased from Merck and Aldrich and used without further purification. Silica sulfuric acid was prepared according to the reported procedure (9). All yields refer to isolated products after purification. Products were characterized by comparison of spectroscopic data (IR, 1H NMR (500 MHz) and 13C NMR (125 MHz) spectra) and melting points with authentic samples. The NMR spectra were recorded on a Bruker Avance DEX 500 and 500 MHz instrument. A Magna-550 Nicolet recorded FT-IR spectra. Spectra of hydrazone were obtained with KBr pellet and CH2Cl2 solvent. Vibrational transition frequencies were reported as wave numbers (cm⁻¹). Mass spectra were recorded on a Shimadzu GCMS-QP5050A benchtop quadrupole mass spectrometer operating at an ionization potential of 70 eV. Melting points were determined in open capillaries with a BUCHI 510 melting point apparatus and are uncorrected. TLC was performed on silica gel polygram SIL G/UV 254 plates.

2.2. Preparation of silica sulfuric acid

A 500 mL suction flask equipped with a constant-pressure dropping funnel and a gas inlet tube for conducting of HCl gas over an adsorbing solution (i.e. water) was used. It was charged with silica gel 60 G for thin-layer chromatography (60.0 g). Chlorosulfonic acid (23.3 g, 0.2 mol) was added dropwise over a period of 30 min at room temperature. HCl gas immediately evolved from the reaction vessel (SCHEME 1).

After the addition was completed the mixture was shaken for 20 min. A white solid of silica sulfuric acid (76.0 g) was obtained. The amount of H⁺ in the silica sulfuric acid was determined by acid-base titration according to the following reaction (Eq. (1)).

\[
\text{SiO}_2 \cdot \text{SiO}_3\text{H} + \text{H}_2\text{O} \rightarrow \text{SiO}_2 \cdot \text{SiO}_3\text{H} + \text{H}_3\text{O}^+ \quad (1)
\]

The liberated H₃O⁺ was titrated by standard NaOH and the amount of H⁺ in silica sulfuric acid was calculated (0.05 g of silica sulfuric acid equal to 0.13 mmol).

2.3. General procedure for the preparation of α-phenylhydrazone-2-ketomethylquinolines

To mixture of (0.3 g) silica sulfuric acid and 1.5 mmol (1.02 g) of sodium nitrite it was added 1.2 mmol of aniline derivatives and 1 mmol of 2-ketomethyl quinoline derivatives. Then mixture was pulverized for 30 min in room temperature. Completion of the reaction was indicated by TLC. After completion, the mixture was washed with CHCl₃ (10 ml) and filtered to recover the catalyst. The solvent was evaporated. The solid product was purified by recrystallization procedure in aqueous EtOH (25%). The desired pure product(s) was characterized by comparison of their physical data with those of known α-phenylhydrazone-2-ketomethyl quinolines.

1. RESULT AND DISCUSSIONS

2-ketomethylquinolines are important component in organic chemistry because of the applications of these compounds in heterocyclic synthesis and chemical transformations (10,14-19). Different kind of 2-ketomethylquinolines were subjected to the α-phenyl hydrazone reaction in the presence of sodium nitrite, derivatives of aniline and silica modified sulfuric acid in dichloromethane (SCHEME 2). α-phenyl hydrazone reaction were perform under mild and completely heterogeneous condition and gave moderate to excellent yields (TABLE 2). When reactions occur at the methylene group, the azo compound formed initially rapidly rearranges to form the α-hydrazoketones[20].

The reported α-phenylhydrazon reaction can be readily carried simply by placing sodium nitrite, derivatives of aniline; silica modified sulfuric acid, 2-ketomethylquinoline, and CH₂Cl₂ as the inert solvent in
a reaction vessel and efficiently stirring the resultant heterogeneous mixture at 50°C temperature for 1 hour and reported same reaction without solvent at room temperature for 30 min under abrasion.

To choose optimum conditions, first we tried to prepare α-phenylhydrazone-2-ketomethylquinoline (entry b) from the reaction of 4-bromoaniline (1.2 mmol), sodiunmnnitrite (1.5 mmol) and 2-ketomethylquinolin (1 mmol) as a model in the absence and presence of silica sulfuric acid by solvent-free conditions (TABLE 1). As shown from TABLE 2, this transformation requires a catalyst and also 0.3 g silica sulfuric acid can be chosen for the preparation of α-phenylhydrazone-2-ketomethylquinolin derivatives.

The initial azo products were converted the corresponding α-hydrazokethones immediately and the products can be isolated by simple filtration and evaporation of the solvent. The results and reactions conditions are given in TABLE 2.

Although the azo coupling also occurs in the absence of silica modified sulfurice acid, the reaction time is very long with lower yield. Therefore, we think that the silica modified sulfurice acid acts as a reaction medium providing a heterogeneous and solvent free effective surface area for in situ generation of HNO$_2$ in low concentrations. It also makes work-up easy.
NO\(^+\) respectively, in-situ, and thus acts as a N\(_2\)O\(_4\) equivalent because a number of reactions are known in which nitrogen tetroxide (N\(_2\)O\(_4\) \(\Leftrightarrow\) NO\(^+\)NO\(_3\)) acts for formation diazonium salts. Therefore, in this paper we show that in situ generation of NO\(^+\) is an effective factor for the azo coupling.

4. CONCLUSION

In summary, an efficient protocol for the preparation of \(\alpha\)-phenylhydrazone-2-ketomethylquinoline derivatives was described. The reactions were carried out under solvent-free conditions with short reaction time and produce the corresponding products in good to excellent yields. The methodology is safer than those using conventional catalysts like H\(_2\)SO\(_4\) and H\(_3\)PO\(_4\) with respect to the amount, hazard and reaction conditions. Also the catalyst could be successfully recovered and recycled at least for three runs without significant loss in activity.

5. ACKNOWLEDGMENTS

Financial support for this work by the research affair of University of Kashan, and University of Isfahan, Iran, is gratefully acknowledgment

6. REFERENCES