Proceeding Paper

Synthesis of Bis-Hydrazine Using Heterogeneous Catalysis †

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Abstract: Hydrazine derivatives are known as an organic compounds group containing C=N-N=C functional groups. This π-conjugated system enables electronic excitation in the visible and near ultraviolet regions. This is of particular interest for many applications, such as corrosion inhibition dye-sensitized solar cells (DSSC), organogels and fluorescent probes for analytical testing. In addition, many hydrazine derivatives show notable biological and therapeutic activities such as treatment of tuberculosis, Parkinson’s disease and hypertension. Schiff bases form an outstanding class of ligands because of their unique properties, such as stability under different conditions, diversity of donor sites, flexibility of synthesis, and formation of ranges in various coordination geometries of a wide range of complexes. Their complexes have received widespread attention due to their wide range of applications, such as catalysis, electrochemistry, biological sciences, optics, guest chemistry and molecular recognition. Therefore, from a theoretical and practical point of view, the synthesis of hydrazine derivatives is an important issue. In the present work, we have described a new, efficient and environment benign synthetic method for the formation of hydrazine derivatives via heterogeneous catalysis starting from ketones.

Keywords: heterogeneous catalysis; Bis-hydrazine; azines; ketazines

1. Introduction

Heterogeneous catalysis is one of the most important industrial processes in chemical manufacturing today. It is based on surface reactions, which require the adsorption of at least one reactant on the catalyst surface [1]. In recent years, the use of heterogeneous catalysts in organic synthesis has aroused great enthusiasm due to its inherent advantages such as easy post-processing, reusability and low cost [2]. As long as the active sites are not deactivated, the heterogeneous catalyst can be easily distinguished from the reaction mixture by simple filtration and reused in subsequent reactions. Heterogeneous catalysis also helps to minimize the waste generated from post-reaction processing and promote the development of green chemical processes [3].

The azines (2,3-diaza-1,3-butadiene) of the formula $R_1R_2C=N-N=N-CR_2R_1$ are a class of functional compounds. They are sometimes called NN-linked diimines (C=NN=C) [4]. They have received more and more attention due to their chemical properties. They facilitate the construction of medically important heterocyclic compounds involving cycloaddition reactions [5–8].

In addition, such compounds have been used to design covalent organic frameworks (COF) [9] and as building blocks of supramolecular chemistry [10,11]. Due to their interesting physical properties, azines have been used as conductive materials [12,13],
ion selective optical sensors [14,15] and nonlinear optical (NLO) materials [16,17]. In addition, azines have potential biological properties (Figure 1), such as antibacterial [18], antihypertensive [19], antifungal [20], antibacterial [21] and anticancer [22] activities. They are useful candidates for drug development in the pharmacology industry.

These compounds are usually synthesized by condensation of hydrazine and aldehyde/ketone [23]. With the latest developments in chemistry, several other methods of synthesizing azines have also been reported [24]. The azines obtained by the condensation of aldehydes and hydrazine are called aldazines, and the condensation products of ketones and hydrazine are called ketazines [25]. In recent years, a transition metal catalysed single-step scheme for the synthesis of azine has attracted much attention. In the present work, a nickel-based heterogeneous catalyst was utilized for the synthesis of Ketazines derivatives with a new, efficient and environment benign synthetic method in a short time at room temperature and resulting high yields.

![Biologically active azines](image)

**Figure 1.** Biologically active azines.

### 2. General Experimental Procedure

A mixture of acetophenone (2.08 mmol) in ethanol (15 mL) was stirred with hydrazine hydrate (1 mmol), and then Ni-based heterogeneous catalyst was added to the mixture with a small amount. The reaction mixture was stirred at room temperature until solidified. The precipitated product was filtered, washed with water and dried then crystallized from ethanol to give (76–89% yield) of ketazines in less than 3 hours (Scheme 1).

![General synthesis pathway of Ketasines using Ni-based heterogeneous catalyst](image)

**Scheme 1.** General synthesis pathway of Ketasines using Ni-based heterogeneous catalyst.

### 3. Results and Discussion

After optimization of the reaction conditions using different solvents in different temperatures it was observed that the condensation of hydrazine hydrate with various acetophenone derivatives 1a-1 proceeded smoothly in the presence of ethanol and Nickel based heterogeneous catalyst at room temperature resulting the formation of ketazines 2a-1 with good to excellent yields in less than three hours (Scheme 2).
In summary, we have reported in this work the synthesis of Ketasines (Bis-hydrazines derivatives) in the presence of Nickel-based heterogeneous catalyst using hydrazine hydrate and various acetophenone derivatives. The reaction was carried out with low catalyst loadings and short reaction times, which represents an economic and environmentally friendly approach.

**References**