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Sunlight assisted synthesis of α-aminonitrile using Capillary flow microreactor: A new approach

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ABSTRACT

The significance of continuous flow capillary reactor in reaction efficiency was investigated using a series of microreactors. We designed and fabricated 3 capillary microreactors starting with 3.0m, 7.5 m and 11.0m, capillary and the difference in efficiency and reduced reaction time was observed. These microreactors were used for the photochemical synthesis of α-aminonitriles. A cheap and readily available cyanide source (KCN) and a photoredox organic catalyst (Rose Bengal) were demonstrated to be vital requisites for this reaction. This reaction was carried out under sunlight irradiation, and excellent yields were recorded. Interestingly, we were able to affirm the effect of capillary reactor length on reaction time as a function of increased resident time of reaction mixture under the sun. The yield was still maintained around 80.6% on average for the three reactors, with the 11.0 m reactor showing the least reaction time of about 24 h. For the first time, we combined an organic dye and acetic acid (cocatalyst) for the synthesis of α-aminonitriles.

1. Introduction

The geographical area between latitudes 40 N and 40 S in the world is referred to as Sun Belt, and Saudi Arabia falls between latitudes 31 N and 17.5 N which is within the world Sun Belt region [1]. Average solar radiation in Saudi Arabia records between a maximum of 8.004 kW/m^2/h at the city of Bisha and a minimum of 4.479 kW/m^2/h at the city of Tabuk. The high solar radiation value >5 kW/m^2/h are experienced in most parts of the country [1].

The emergence of continuous flow chemistry has been the main focus in photochemistry. The combined system of microreactors and flow operations has proven to be an irrefutable idea in photochemical applications in this era [2]. An efficient and homogenous light penetration is achieved via the narrow reaction channels and yield improvement in shorter time. Photochemistry in the lab has been the traditional approach to photochemical reactions using artificial light sources such as LEDs, fluorescent bulbs etc. The cost and lengthy reaction time have drifted the idea to the use of sunlight as a source of light for the initiation of the applications in question [3]. In the literature, it has been established that solar photochemical reactions are independent of temperature that is, the effect is negligible. However, it strongly depends on the intensity [4].

α-Aminonitriles are known to be an essential category of so many intermediates for an extensive variety of biological products and pharmaceuticals since α-amino acids are produced from the hydrolysis of the nitrile function [5]. Also, the hydrogenation of nitriles yields useful 1,2-diamines. Countless hard work has been dedicated to the improvement of new approaches for the production of α-aminonitriles [6]. Amongst the various methods known for the synthesis is the oxidative cyanation of sp^3 C—H adjacent to the nitrogen atom which represents one of the best approaches to prepare these compounds [7]. Earlier works showed the formation of reactive iminium ion intermediates by treating tertiary amines with various metal catalysts in the presence of stoichiometric amounts of oxygen which is intercepted with HCN to give the equivalent α-cyanation product [5].

Rueping et al. [5] carried out this type of reaction using a cyclic amine, tetrahydroisoquinoline derivatives, an inorganic iridium-based poly pyridyl complex [Ir(tbp-py)$_2$(bpy)]PF$_6$] where "tbp-py" stands for 2-(4-tBu-phenyl)-pyridine, as a catalyst, acetic acid as a co-catalyst, and reaction was irradiated under 5 W fluorescent bulb. They were able to isolate the corresponding product with about 96% yield after 20 h of reaction. Subsequently, in the same report, they carried out the same reaction under the same condition but using an acyclic amine, and recorded a yield of about 82% after 12–96 h [3].

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In this work, we focused more on the robustness of our device, the fabricated flow microreactor and employed for the reaction in question under sunlight irradiation. The concept was to develop and relate how increasing the size of the capillary will enhance the efficiency of reaction via increased exposure as well as reaction residence time under sunlight irradiation. In the design of our device, so many factors were put in place to ensure better efficacy. The reactor must show minimal clogging and crystallization, high transparency to light for optimum penetration, larger surface area for maximum light required for reaction initiation and the type of glass material [8]. We chose quartz as the glass material type following its cutoff wavelength of <170 nm (enough energy) to break C—H bonds [9]. Following the success of the reactor design, we employed the reactor for the cyanation reaction using acyclic amine. In order to avoid the use of expensive inorganic catalysts like the iridium complex, we focused on using an organic dye Rose Bengal which is known for its effectiveness as a sensitizer in this type of reactions. Also to cut cost, we carried out the reaction under sunlight.

In our work, a lux meter was used for an onsite measurement of sunlight intensity in the kingdom with direct sunlight registering about 5.26 kWh/m^2/day from September to November (2015) and the coudy daylight recorded about 3.72 kWh/m^2/day from December (2015) to March (2016). During this period, temperature ranged 38 °C to 20 °C for September and March respectively.

2. Materials and methods

2.1. Chemicals and materials

Rose Bengal (≥90%), was purchased from Sigma Aldrich. Acetonitrile (UHPLC Super grade 99.9%) was purchased from Panreac AppliChem Company. KCN (99 +%), was purchased from Alfa Acsar, Acetic acid (>99.5%) was purchased from Fluka Chemica, Ethyl acetate (99.9%) from Analar Normapur and Hexane (99 +%) was purchased from Sigma Aldrich. All the solutions were prepared with deionized water (Siemens Ultra-clear, Saudi Arabia).

Column chromatography was carried out on silica gel with hexane/ethyl acetate (3:1). Joel company brand NMR was used for this study: ^{1}H NMR spectra were recorded on 500 MHz in $CDCl_3$ and ^{13}CNMR spectra were recorded on 125.6 MHz in $CDCl_3$.

2.2. Reactor fabrication and setup

We designed and fabricated a capillary flow microreactor for an efficient continuous flow using a commercially available glass material, quartz. The following requirements were put into place before we could design the reactors:

The reactor must show minimal clogging and crystallization, transparent to light for optimum penetration, larger surface area for maximum light required for reaction initiation and the type of glass material. Quartz glass has the least cut-off wavelength of about <170 nm which is sufficient enough to break the C—H bond necessary for the reaction to proceed [10]. The three fabricated capillary flow reactors of 3.0, 7.5 and 11.0 m are shown in Fig. 1 below.

2.2.1. Fabrication

A capillary tube with a diameter of 0.2 mm was bent into the shape of interest using hydrogen flame, which was then connected to the reaction mixture via a tube. The tube was passed through the pump which ensures a continuous flow of reaction from the mixture through the capillary reaction. The same procedure was repeated during the fabrication of subsequent reactors used for this study.

Following the advantages of continuous flow methods over the traditional batch reaction, higher interest has been shown in this approach. Some of the advantages include; reproducibility, control of reaction parameters with precision, efficient energy and ease to scale-up reactions [11]. In this regard, the efficient conversion may

Fig. 1. Fabricated capillary reactors for 3.0, 7.5 and 11.0 m employed for the experiments.