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Synthesis of organosilyl compounds-containing 1,2,4,5-tetraaryl imidazoles sonocatalyzed by M/SAPO-34 (M = Fe, Co, Mn, and Cu) nanostructures

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ABSTRACT

The one-step synthesis of silylated 1,2,4,5-tetraaryl imidazoles by use of a series of M/SAPO-34 (M: Fe, Co, Mn, and Cu) nanocatalysts and subsequent silylation reactions is described. Cu/SAPO-34 catalyst has the highest activity in improving the efficiency of the heterogeneous cyclo-condensation of an aldehyde, benzil, ammonium acetate and a primary aromatic amine in water under ultrasonic irradiation. Some of imidazole derivatives are studied with a view to the synthesis of a series of new, multi-substituted imidazoles containing organosilyl groups including carbosilanes (Si–C) and silyl ethers (Si–O).

1. Introduction

The chemistry of organosilicon compounds can provide a wealth of chemical and biological diversity for medicinal drugs design. The incorporation of silicon atom into a drug structures has been used to improve pharmacological potency, to modify selectivity toward a given target, to change metabolic rates, and specifically to increase lipophilicity. A small increase in lipophilicity can provide several physiological benefits, including increased bio-availability as well as tissue and cell penetration [1–3]. Some of silicon-containing drug structures such as Tac101 and BNP1350 have entered human clinical trials for the treatment of cancer [2] (Fig. 1).

The imidazole core constitutes an active backbone in exciting medications and is present in natural products, e.g., Losartan, Olmesartan, Eprosartan, Pimobendan, Trifenagrel, and Naamidine A (Fig. 2). The potency and wide applicability of the imidazole pharmacophore can be attributed to its hydrogen bond donor–acceptor capability as well as its high affinity for metals that are present in many protein active sites. Some of imidazole derivatives could be used as ionic liquids, anion sensors, electrical and optical materials, in molecular switches and organic light-emitting diodes (OLEDs). This versatile applicability highlights the importance of access to efficient synthetic routes to well benign fully substituted imidazoles [4–9]. Cyclizations via one-pot multicomponent coupling reactions (MCRs) are widely used for eco-compatible syntheses [10].

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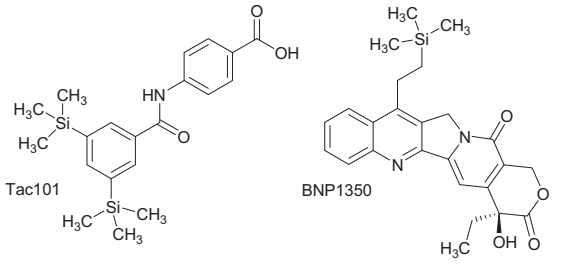

Fig. 1. Potent silicon-based drugs.

Multisubstituted imidazoles are generally synthesized by one-step condensation of an aldehyde, benzil, ammonium acetate and primary aromatic amine in the presence of various catalysts and green techniques [8,11–13]. Now, the use of ultrasound irradiation in different areas of chemistry has grabbed significant levels, not only for the possibility to perform environmentally benign syntheses, but also for the excellent yields they allow [14–18]. Many organic reactions have been devised, in which reagents are supported on various inorganic solid supports [19]. Various metal-supported zeolites, such as Cu-modified zeolites (HY, H–USY, H–Beta, Mordenite and ZSM-5), have been given more attention for catalytic applications [20]. Recently, silicoaluminophosphate (SAPO-*n*) zeolites, as small pore-sized molecular sieves, have been successfully used by several industrial researchers [21–23]. No reports are available on the synthesis of fully substituted imidazoles by use of H-SAPO-34 zeolites. Therefore, investigation of the preparation of tetraaryl imidazoles using M/SAPO-34 (M: Fe, Co, Mn, and Cu) zeolite catalysts as heterogeneous "E" catalysts (efficient, eco-friendly and economic) via zeolite-catalyzed multicomponent reactions (ZCMCRs) [24] was carried out in this study. In continuation of our interest in the synthesis of useful heterocyclic compounds possessing an imidazole nucleus and because of the importance of organosilicon compounds, we have synthesized a series of new, multi-substituted imidazoles containing organosilyl groups including carbosilanes (Si–C) and silyl ethers (Si–O).

2. Results and discussion

The catalytic influence of the different transition metals supported on the H-SAPO-34 zeolite, of the weight loadings of metal (wt.%), of the amount of catalysts has been studied here with different reaction media that were tested for the preparation of highly substituted imidazole derivatives. A one-pot four-component condensation of benzil (1 mmol), benzaldehyde (1 mmol), *p*-methylaniline (1 mmol), and ammonium acetate (1.1 mmol) was used as a model reaction for the synthesis of 2,4,5-triphenyl-1-*p*-tolyl-1*H*-imidazole **1a** in water under ultrasound irradiation (high intensity). In the absence of a catalyst, the reaction was incomplete, even after 2 h of sonication, though the formation of a small amount of **1a** (20%) was observed. When the model reaction was carried out in the presence of an H-SAPO-34 support (10 wt.%) in the same conditions, the product **1a** was isolated with 32% yield, after 60 min. However, the reaction proceeded rather slowly and no significant acceleration was observed. We showed that the incorporation of different transition metals into the H-SAPO-34 support improves the cyclocondensation reaction leading to the synthesis of a series of M/SAPO-34 (M: Fe, Co, Mn, and Cu) catalysts. All catalysts showed good yield and only produced trace amounts of by-product 2,4,5-triphenyl-1*H*-imidazole, at Mn-based catalyst. Metal loading on the support was done at two different loading of 5.0 and 10 wt.% of metal on the support. The results showed that the activity of catalysts with a metal loading of 10 wt.% is lower with a 5 wt.% loading. This decrease can be attributed to excessive metal agglomeration, leading to the formation of large metal particles. In addition, further content of metal blocks the pores and the active sites of the catalyst so that catalytic activity decreases. The best results (95% yield, after 3 min) were obtained in the presence of 5 wt.% of Cu/SAPO-34 in aqueous medium

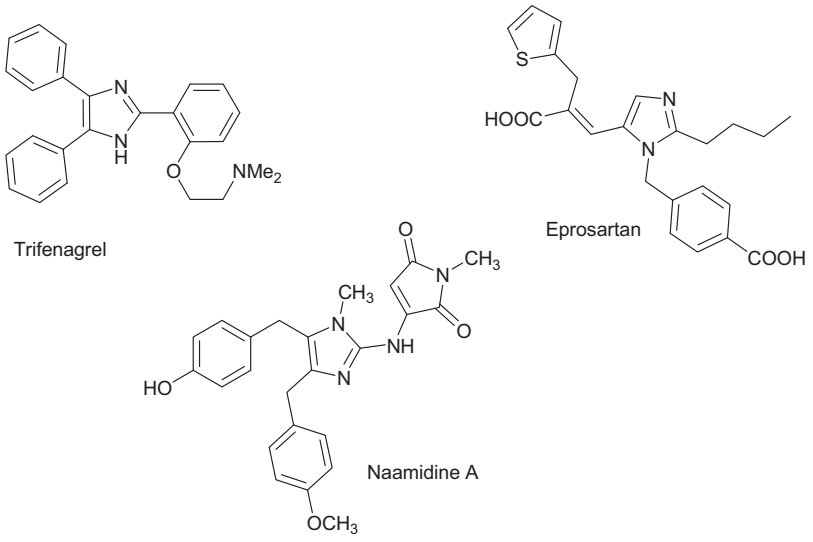

Fig. 2. Potent imidazole-based drugs.