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ORIGINAL ARTICLE

An efficient multi-component synthesis of 14-aryl-14*H*-dibenzo[a,j]xanthene derivatives by AgI nanoparticles

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KEYWORDS

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Abstract Recoverable heterogeneous AgI nanoparticles efficiently catalyzed the one-pot synthesis of 14-aryl-14*H*-dibenzo[a,j]xanthenes *via* multi-component reaction of aldehydes and 2-naphthol under solvent-free conditions. The present approach offers several advantages such as short reaction times, high yields, easy purification, reusability of the catalyst and low catalyst loading.

1. Introduction

Multi-component reactions (MCRs) have emerged as an efficient and powerful tool in modern synthetic organic chemistry allowing the facile creation of several new bonds in a one-pot reaction (Nakamura and Yamamoto, 2004). Clearly, for multi-step synthetic procedures a number of reactions and purification steps are among the most important criteria for the efficiency and practicability of the process and should be as low as possible. The strategy of MCRs especially for the preparation of heterocyclic compounds is a particularly attractive field in light of the paramount role of these targets in pharmaceutical chemistry (Negwar, 1994).

The synthesis of xanthene derivatives has been received special attention to chemists because of their wide range of therapeutic and biological properties, such as antibacterial (Lambert et al., 1997), antiviral (Hideo and Teruomi, 1981) and anti-inflammatory activities (Hafez et al., 2008). In addition, these compounds have found wide applications in dyes (Menchen et al., 2003), laser technologies (Ahmad et al., 2002) and as pH-sensitive fluorescent materials for visualization of biomolecules (Knight and Stephens, 1989). There are several methods reported in literatures for the synthesis of xanthene derivatives including the reaction of aryloxy magnesium halides with triethyl orthoformate (Casiraghi et al., 1973), cyclodehydration (Bekaert et al., 1992), trapping of benzynes by phenols (Knight and Little, 2001), intermolecular phenyl carbonyl coupling reactions of benzaldehydes and acetophenones (Kuo and Fang, 2001), cyclization of polycyclic aryl triflate esters (Wang and Harvey, 2002) and cyclocondensation between 2-hydroxy aromatic aldehydes and 2-tetralone (Jha and Beal, 2004). Although, the preparation of xanthenes has been achieved via the reaction of various aldehydes and 2-naphthols by cyclodehydration in the presence of diverse catalysts, such as AcOH–H_2SO_4 (Sarma and Baruah, 2005), *p*-TSA

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(Khosropour et al., 2005), $MeSO_3H$ (Bhattacharya and Rana, 2007), sulfamic acid-ionic liquid (Wu et al., 2009), iodine (Das et al., 2006; Fei-Qing et al., 2007), heteropoly acid (Mohammadpour et al., 2007), silica sulfuric acid (FischerHunnur et al., 2008), amberlyst-15 (Ko and Yao, 2006), cyanuric chloride (Bigdeli et al., 2007), LiBr (Saini et al., 2006), $CoPy_2Cl_2$ (Madhav et al., 2008), $Yb(OTf)_3$ (Su et al., 2008), $Sc[N(SO_2C_8F_{17})_2]_3$ (Hong and Cai, 2009), $NaHSO_4$ (Jaberi and Hashemi, 2008), $Al(HSO_4)_3$ (Shaterian et al., 2007), P_2O_5 or $InCl_3$ (Kumar et al., 2010), tetra-*n*-butylammonium bromide (TBAB) (Kantevari et al., 2008), nano-TiO_2 and BF_3–SiO_2 (Mirjalili et al., 2008, 2011). Consequently, the synthesis of benzoxanthene derivatives, with the aim of developing new drug molecules has been an active area of research. Much attention has been paid to the development of new methodologies for the preparation of 14-aryl-14*H*-dibenzo[a,j] xanthenes.

Nanotechnology has been one of the most active research areas in recent years. The reactivity of catalytic nanoparticles is largely determined by the energy of surface atoms, which can be easily gauged by the number of neighboring atoms by the bonding modes and accompanying energies of small molecules to be transformed on the nanoparticles surface (Min et al., 2008). Due to the non-additive nature of the catalytic properties of nanoparticles, research in the field of nanoparticles based catalysis has been focused onto the preparation of small nanoparticles with high surface-to-volume ratios for high catalytic activity. Several reports showed an amazing level of the performance of nanoparticles as catalysts in terms of selectivity, reactivity, and improved yields of products (Astruc et al., 2005).

Among various metal nanostructures, silver nanoparticles have received considerable attention because of their unusual properties and potential applications in diverse fields (McFarland and Van Duyne, 2003). silver iodide nanoparticles, in particular, being available, require only mild reaction conditions to produce high yields of products in short reaction times compared to traditional catalysts and can also be recycled (Astruc, 2008). Recently, silver nanoparticles were used as an active catalyst in many reactions including three-component coupling of aldehyde–amine–alkyne (Zhou et al., 2008), carbon–carbon coupling reaction (Murugadoss et al., 2009), dehydrogenation reaction (Shimizu et al., 2009), oxidation reaction (Mitsudome et al., 2008), Diels–Alder cycloadditions of 2′-hydroxychalcones (Cong et al., 2010) and synthesis of β-enaminones (Kushal et al., 2010).

In order to improve more efficient synthetic procedures, reduce the number of separate reaction steps and minimize by-products, here we report a novel and mild method for the preparation of xanthenes via multi-components coupling of 2-naphthol and aryl aldehydes in the presence of silver iodide nanoparticles (Scheme 1). In the view of recent interest in the use of heterogeneous catalysts we have developed AgI nanoparticles as an inexpensive, non-volatile, recyclable, non-explosive, easy to handle and eco-friendly catalyst which can be used in the catalysis of many organic reactions.

2. Experimental

2.1. Materials and methods

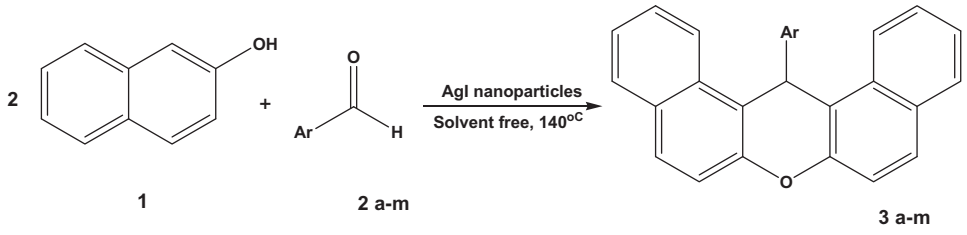
Chemicals were purchased from the Sigma–Aldrich and Merck in high purity. All of the materials were of commercial reagent grade and were used without further purification. All melting points are uncorrected and were determined in capillary tube on Boetius melting point microscope. ^1H NMR and ^{13}C NMR spectra were obtained on Bruker 400 MHz spectrometer with $CDCl_3$ as solvent using tetramethylsilane (TMS) as an internal standard, the chemical shift values are in δ. FT-IR spectrum was recorded on Magna-IR, spectrometer 550 Nicolet in KBr pellets in the range of 400–4000 cm^{-1}. The elemental analyses (C, H, N) were obtained from a Carlo ERBA Model EA 1108 analyzer. Powder X-ray diffraction (XRD) was carried out on a Philips diffractometer of X'pert Company with monochromatized Ag Kα radiation (λ = 1.5406 Å). Microscopic morphology of products was visualized by SEM (LEO 1455VP). The mass spectra were recorded on a Joel D-30 instrument at an ionization potential of 70 eV.

2.2. Preparation of silver iodide nanoparticles

A solution of 0.415 g KI (25×10^{-4} mol) in 25 mL distillated water was added drop wise to $AgNO_3$ solution (0.425 g, 25×10^{-4} mol in 25 mL distillated water) under ultrasound power in the presence of 0.2 g SDS as surfactant. The yellowish as-synthesized precipitate was separated by centrifugation and washed with distillated water and ethanol for several times to remove impurities and then dried.

In order to investigate the morphology and particle size of AgI nanoparticles, SEM image of AgI nanoparticles was presented in Fig. 1. These results show that spherical AgI nanoparticles were obtained from $AgNO_3$ and KI with particle size in the range of 40–50 nm under ultrasound power.

Fig. 2 shows the FT-IR spectrum of AgI nanoparticles. The broad peak at 3436 cm^{-1} and 1628 cm^{-1} can be attributed to the *v* (OH) stretching and bending vibrations, respectively. Therefore, these peaks indicate the presence of physisorbed water linked to nanoparticles, the peak corresponding to CH_2 stretching vibration of SDS (sodium dodecyl sulfonate) at 2923 cm^{-1} can be seen. The appearance of this peak suggests that a trace amount of SDS has been coated on the surface of AgI nanoparticles.



Scheme 1 One-pot synthesis of xanthene derivatives in the presence of silver iodide nanoparticles under solvent-free conditions.