ARTICLE IN PRESS

Journal of Saudi Chemical Society (2012) xxx, xxx–xxx

King Saud University

Journal of Saudi Chemical Society

www.ksu.edu.sa
www.sciencedirect.com

ORIGINAL ARTICLE

Green synthesis of 1,4-quinone derivatives and evaluation of their fluorescent and electrochemical properties

Palanisamy Ravichandiran [a], Ramanujam Kannan [a,b], Alagunambi Ramasubbu [c], Shanmugam Muthusubramanian [d], Vasanth Kumar Samuel [a,b,*]

[a] *Department of Chemistry, School of Science & Humanities, Karunya University, Coimbatore 641 114, India*
[b] *Department of Nanosciences & Technology, School of Nanosciences & Technology, Karunya University, Coimbatore 641 114, India*
[c] *PG & Research Department of Chemistry, Government Arts College (Autonomous), Coimbatore 641 018, India*
[d] *Department of Organic Chemistry, School of Chemistry, Madurai Kamaraj University, Madurai 625 021, India*

Received 20 June 2012; accepted 10 September 2012

KEYWORDS

Microwave;
Water as solvent;
Dapsone;
Cyclic voltagram

Abstract Green synthesis of some 1,4-quinone derivatives by conventional and solvent free microwave assisted methods has been reported. The microwave assisted method resulted in higher percentage yield at shorter time compared to the conventional one. In the conventional method environmentally friendly solvent was used and the results were compared with other solvents. When water was used as a solvent the reaction exhibited higher yield than other solvents like ethanol. The solvent free method under microwave irradiation method yielded the highest yield compared to the conventional methods. The resultant compounds were analyzed by UV–Vis, FT-IR, ^{1}H and ^{13}C NMR spectroscopy. The synthesized quinone derivatives exhibited the fluorescent and electrochemical properties.

1. Introduction

Quinones are large group of natural pigments that show excellent photochemical properties (Bruce and Patai, 1974) and act as an intermediate in the biosynthesis of important antibiotics (Bentley et al., 1974). They exhibit a number of biological activities which include antidiabetic (Zhang et al., 1999), anticancer (Kinugawa et al., 1996), cytotoxic (Jonathan et al., 1989), enzyme inhibitory (Puder et al., 2005) and antioxidative activities (Lee et al., 1996). They have also been used as charge-transfer complexes (Murata et al., 2004) and chemical sensors (Nam et al., 1999). The property that undergoes the change from hydroquinones to quinones, plays an important role in the redox processes that occur in living organisms. They also act as electron–proton carriers for carrying oxygen in biochemical reactions (Khan and Choudhury, 2010) (see Figs. 1 and 2).

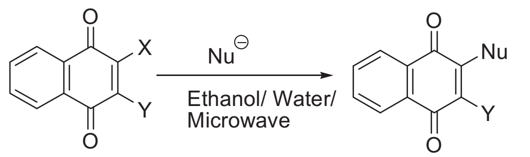
Green chemistry is a new and fast developing field of synthetic chemistry. Its objective of utilizing resources is aimed at reducing as much chemical waste as possible at the same time minimizing the pollution and this has garnered much attention in recent years (Redasani et al., 2010).

* Corresponding author. Address: Department of Chemistry, School of Science & Humanities, Karunya University, Karunya Nagar, Coimbatore 641114, Tamil Nadu, India. Tel.: +91 9442429024; fax: +91 422 2615615.
E-mail address: kumar2359@yahoo.com (V.K. Samuel).

Peer review under responsibility of King Saud University.

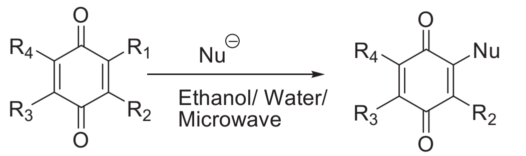
ELSEVIER Production and hosting by Elsevier

1319-6103 © 2012 King Saud University. Production and hosting by Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jscs.2012.09.011



X,Y=Cl
X,Y=H

Figure 1 1 Nucleophilic addition and substitution reaction of 2,3-dichloro-1,4-naphthaquinone and 1,4-naphthaquinone.



R1-R4 =Cl
R1-R4 =H

Figure 2 Nucleophilic addition and substitution reaction of tetrachloro benzoquinone and 1,4-benzoquinone.

To reduce pollution due to hazardous chemicals, emphasis should be given to the development of greener approaches (Jalani et al., 2012). The most abundant and available resource on the planet is the aqueous medium, water in which biochemical processes take place. Water has been recognized as an eco-friendly solvent in organic chemistry for a long time. In addition to its environmental benefits, the use of water as a solvent is both inexpensive and safe. In recent decades, the study of organic reactions in aqueous solvent has accelerated and often surprising discoveries have been made (Witayakran and Ragauskas, 2007). A number of nucleophilic addition/substitution reactions have been reported in water with substantial rate acceleration even when water insoluble substrates were used as suspensions (Tandon and Maurya, 2009).

Microwaves synthesis has become a well established technique in chemistry that has found wide applications in the laboratory as well as in industries. Nowadays a number of articles have been published in the field of microwave assisted organic syntheses (Solhy et al., 2011). It is extensively employed for the synthesis of new drug molecules and other pharmaceutical intermediates (Hayes, 2004). And it has the distinct advantage of enhanced yield of product and rapid reaction rates (Omprakash et al., 2010), because of the shorter duration of chemical transformations (Castro et al., 2011).

Quinone and its derivatives are known to be photo and electro chemically active molecules. They find extensive applications in the areas of fabrication of chemical transducers and molecular switch systems (Illos et al., 2006). Fluorescent heterocyclic compounds are widely used in many fields like making of emitters in electroluminescence devices, as probes in biochemical research. These compounds are also employed as photo-conductive materials (Dabiri et al., 2001).

In this communication, we report the green synthesis of 1,4-quinone derivatives by conventional heating methods using water and ethanol as solvents. The same compounds were also synthesized under solvent free condition assisted by microwave irradiation. All the compounds were characterized by ultra violet–visible (UV–Vis), fourier transform infrared (FT-IR), proton (^{1}H) and carbon (^{13}C) NMR spectroscopies. The electrochemical and photochemical properties of the synthesized compounds were studied and reported.

2. Experimental

Melting points (°C, uncorrected) of the synthesized compounds were checked in open capillary tubes by using a digital auto melting point apparatus (Labtronics 110, India) and found uncorrected. All the chemicals and solvents were purchased from Sigma–Aldrich and Merck, India. All the reactions were checked by thin layer chromatography (TLC silica gel 0.25 mm, 60 G F254 and eluting solvents were ethyl acetate: hexane 1:1). The synthesized compounds were purified by column chromatography using column silica gel 100–200 mesh (ethyl acetate: hexane 1:2). All the compounds were characterized by UV–Vis spectrophotometer (UV-1800, Shimadzu, Japan) using acetone as solvent, FT-IR spectrometer (IR 8400, Shimadzu, Japan) using KBr pellets, ^{1}H NMR spectroscopy in DMSO (400 MHz, Bruker), and ^{13}C NMR spectroscopy in DMSO (400 MHz, Bruker) using tetramethylsilane (TMS) as internal standard. Microwave assisted synthesis was carried out using a domestic microwave oven (LG, MH 6558 BH, 50 HZ, 1350W). The fluorescence properties of compounds 1–6 were studied using acetone as solvent in a fluorescence spectrophotometer (FP 8200, Jasco, Japan). Electrochemical studies were carried out using an electrochemical workstation (CH Instruments, Inc., CH1660C, USA).

2.1. General procedure for conventional and microwave assisted synthesis (compounds 1–6) conventional heating method (method-I)

A mixture of 2,3-dichloro-1,4-naphthaquinone (0.227 g, 0.01 mol.) and dapsone (0.248 g, 0.01 mol.) was added to ethanol (100 mL) and the solution was refluxed for 5 h at 60 °C. The resulting solution was cooled and the precipitate was filtered, dried at room temperature and purified by column chromatography. The other compounds (2–6) were also synthesized similarly.

2.2. Conventional heating method (method-II)

A mixture of 2,3-dichloro-1,4-naphthaquinone (0.227 g, 0.01 mol.) and dapsone (0.248 g, 0.01 mol.) was added to water (250 mL) and the solution was refluxed for 3 h at 70 °C. The solution was cooled and the precipitate was filtered, dried at room temperature and purified by column chromatography. The other compounds (2–6) were also synthesized similarly.

2.3. Microwave assisted method (method-III)

A mixture of 2,3-dichloro-1,4-naphthaquinone (0.227 g, 0.01 mol.) and dapsone (0.248 g, 0.01 mol.) was ground together and irradiated in a domestic microwave oven for 10 s/cycle (1350 W). The duration of irradiation varied depending on the degree of completion of the reaction (40–