



ORIGINAL ARTICLE

1,7-Sigmatropic rearrangement in 1,2-dihydro and 1,2,3,4-tetrahydroquinoline synthesis using marine sponge/ $\text{H}_2\text{C}_2\text{O}_4$ as a catalyst



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Received 26 July 2011; accepted 12 June 2012

Available online 25 June 2012

KEYWORDS

Tetrahydroquinoline;
1,7-Sigmatropic rearrangement;
Chirality;
Imino Diels–Alder;
Marine sponge/oxalic acid

Abstract Marine sponge/oxalic acid was found to be an efficient catalyst for the imino Diels–Alder reaction of synthesized *N*-aryl-substituted aldimines and various alkenes to provide 1,2-dihydro and 1,2,3,4-tetrahydro-quinolines using 1,7-sigmatropic rearrangement with induction of chirality. Mild reaction conditions, simple experimental procedure, good yields of products, and optical active induction render this new method attractive for 1,7-sigmatropic rearrangement of imino Diels–Alder reaction.

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1. Introduction

Tetrahydroquinoline and quinoline derivatives are widely found in many natural products, which exhibit various biological and pharmaceutical activities (Aslokar et al., 2004; Omura and Nakagama, 1981; Kumar et al., 2004; Smith et al., 2003; Teimouri et al., in press; Sarveswari et al., in press; Khabaz-zadeh et al., in press; Leeson et al., 1992; Katritzky et al., 1995; Kametani et al., 1986; Babu et al., 1999). For the synthesis of tetrahydroquinolines, the imino Diels–Alder reaction

(povarov) of *N*-arylimine with olefins is highly efficient (Scheme 1) (Jorgensen, 2000; Zhang et al., 2005; Kouznetsov et al., 2006; Zhou and Xu, 2008; Kamble et al., 2010; Buonora et al., 2001; Benforouz and Ahmadian, 2000; Kouznetsov et al., 1998; Kouznetsov, 2009).

Lewis acids like $\text{BF}_3\text{-Et}_2\text{O}$, montmorillonite K-10 clay, CAN, and protic acids such as TFA, *p*-TsOH, oxalic acid, I_2 , KHSO_4 , etc. (Kametani et al., 1985; Ma et al., 1999; Babu and Perumal, 1997; Zhang and Li, 2002; Yadav et al., 2001; Mahesh et al., 2004; Kouznetsov et al., 2004; Maiti and Kundu, 2006; Hadden and Stevenson, 1999; Makioka et al., 1995; Kobayashi et al., 1995; Yadav et al., 2002; Sridharan et al., 2007; Boger and Weinreb, 1987; Mellor et al., 1991; Grieco and Bahasas, 1988; Nagarajan and Perumal, 2001; Xia and Lu, 2005; Kumar et al., 2004; Anniyappan et al., 2002) and silica compounds such as $\text{HClO}_4\text{-SiO}_2$, SBA-Pr- SO_3H (Kamble et al., 2010; Mohammadi Ziarani et al., in press; Kouznetsov

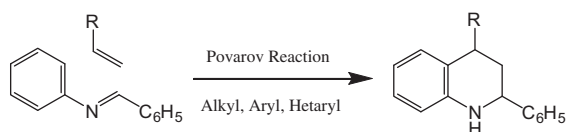
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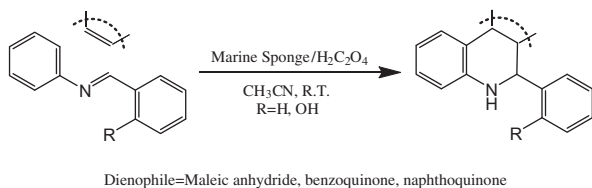
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Scheme 1 General imino diels-alder reaction.



Scheme 2 Marine sponge/ $\text{H}_2\text{C}_2\text{O}_4$ catalysed.

et al., 2007; Zhang et al., 2002; Powell and Batey, 2003; Han et al., 2006; Khan et al., 2011; Byrne and Evans, 2008; Xue et al., 2009) have been found to catalyze these reactions. However, most of these methods involve expensive and more than stoichiometric amounts of Lewis acids which are required due to coordination of the Lewis acids to imine nitrogen, with longer reaction times and strong acidic conditions. In recent years, great efforts have been made to develop organic reactions in an environment-friendly manner (green chemistry).

Marine sponges are known as a prolific source of biologically active and structurally unique metabolites. They are known to produce a large number and diversity of secondary metabolites (Rifai et al., 2005; McCaffrey and Endean, 1985). As there is no report of marine sponges of Iranian coast of Persian Gulf, we studied shallow sponges (*Desmospongia* sp.) of Qeshm Island in offshore zone which can be the source of new biological active compounds. In organic chemistry, these sponges are important and optical active source for catalytic reactions such as oxidation, reduction etc. (Sarma et al., 2005). The chiral non-racemic catalyst, marine sponge, which has optical active compounds such as alkaloids, terpenoids, is the good catalyst for induction of chirality into desired products with excellent enantioselectivities in 1,2,3,4-tetrahydroquinolines synthesis. The chiral and acidic marine sponge can activate the C–N bond for nucleophilic addition with high and predictable asymmetric induction, and is easily removed from the product. Therefore, the search continues for a better catalyst in 1,2,3,4-tetrahydroquinolines synthesis in terms of operational simplicity, with greater yields and in particular, excellent enantioselectivities.

In the course of our studies for C–C bond formation (Shushizadeh and Kiany, 2009) and development of useful synthetic methodologies, we have designed and synthesized a series of new compounds containing the 1,2,3,4-tetrahydroquinolines derivatives using 1,7-sigmatropic rearrangement of imino Diels–Alder reaction (Scheme 2).

2. Experimental

All starting materials were purchased from Merck and Aldrich Companies. The IR spectra were recorded on a Perkin-Elmer RXI infrared spectrometer. ^1H NMR spectra were recorded with a 400 MHz Bruker ft-nmr spectrometer. TLC accomplished the purity of substrates and reactions were monitored

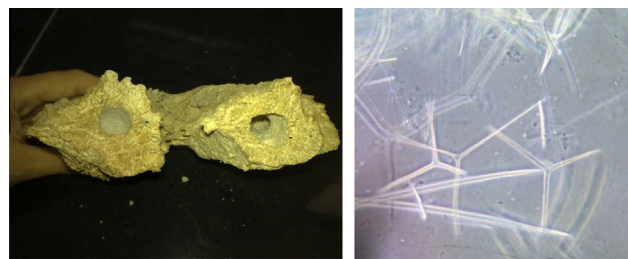


Figure 1 (a) Marine sponge (*Demospongiae* sp.); (b) *Siliceous spicules*.

on silica gel polygram SIGL/UV254 plates. Melting points reported were determined by open capillary method using a Mettler melting point apparatus and are uncorrected.

The marine sponge (*Demospongiae* sp.) was used as solid supported with oxalic acid for transformation of acidity and chirality in reaction media and products. Samples were collected in May 2010 at a depth between 5 and 10 m in the Nakhiloo Island, Bushehr, Iran (North coast of Persian Gulf) and were washed several times using deionized water to remove extraneous and salts. They were then dried in an oven at 60 °C for 48 h. The dried marine sponge chopped, sieved and the particles with an average size of 0.5 mm were used for acid catalyzed experiments. Identification of sponges was carried out kindly by Dr. Sayed Mohammad Bagher Nabavi. The species investigated in this study are *Demospongiae* sp. (Fig. 1a) which has siliceous (SiO_2) spicules (Fig. 1b).

2.1. General procedure

Imines were prepared by the standard procedure of refluxing equimolecular amounts of the suitable aniline and aldehyde in ethanol for 3–4 h and filtering the solid that precipitated after cooling (Chakraborti et al., 2004; Guzen et al., 2007)¹. The suitable imine (2 mmol) was dissolved in acetonitrile (15 mL). To this stirred solution was added the solution of 2.5 mmol of dienophile and marine sponge/ $\text{H}_2\text{C}_2\text{O}_4$ (50 mg,

¹ Selected spectral data for some imines in Table 1 are given: (*E*)-*N*-benzylideneaniline (**1a**) Chakraborti et al., 2004; Guzen et al., 2007: IR(cm^{-1} , KBr): 1610 (C=N), 1520 (C=C), 1232, 1033, 790 cm^{-1} . ^1H NMR (400 MHz, CDCl_3 , TMS, δ ppm): 8.40 (1H, s), 7.72 (2H, d), 7.62 (2H, d), 7.51 (1H, t), 7.4–7.2 (5H, m); ^{13}C NMR (400 MHz, CDCl_3 , TMS, δ ppm): 160 (HC=N), 152, 137.4, 132.2, 128(6C), 125.1, 120. (*E*)-2-((phenylimino)methyl)phenol (**1d**) Chakraborti et al., 2004; Guzen et al., 2007: IR(cm^{-1} , KBr): 3421 (–OH), 1600 (C=N), 1550, 1520 (C=C), 1222, 1033, 850, 760. ^1H NMR (400 MHz, CDCl_3 , TMS, δ ppm): 12.4 (1H, bs), 8.50 (1H, s), 7.8 (2H, d), 7.72 (1H, d), 7.61 (1H, t), 7.3–7.0 (5H, m); ^{13}C NMR (400 MHz, CDCl_3 , TMS, δ ppm): 162 (HC=N), 158, 147.1, 132(2C), 129(2C), 125, 119(3C), 117.9, 115. (*E*)-*N*-benzylidene-4-methoxybenzenamine (**1e**) Chakraborti et al., 2004; Guzen et al., 2007: IR(cm^{-1} , KBr): 1504, 1251, 1033, 831. ^1H NMR (400 MHz, CDCl_3 , TMS, δ ppm): 8.20 (1H, s), 7.16 (2H, d), 6.83 (2H, d), 6.43–7.49 (5H, m), 3.72 (3H, s); ^{13}C NMR (400 MHz, CDCl_3 , TMS, δ ppm): 158.4 (HC=N) 152.2, 145.6, 145.2, 144.2, 122.2, 115.5, 114.3, 112.0 (2Ar, 12C), 55.3 (OMe). (*E*)-*N*-benzylidene-4-nitrobenzenamine (**1f**) Chakraborti et al., 2004; Guzen et al., 2007: IR(cm^{-1} , KBr): 3073, 2348, 1869, 1531, 1118. ^1H NMR (400 MHz, CDCl_3 , TMS, δ ppm): 8.65 (1H, s), 8.38 (1H, s), 8.16 (1H, d), 8.10 (1H, d), 7.50 (1H, t), 7.62–7.11 (5H, m); ^{13}C NMR (400 MHz, CDCl_3 , TMS, δ ppm): 162.2 (HC=N), 157.3, 151.0, 138.0, 134.3, 130.5, 130.0, 129.5, 127.0, 125.7, 123.6, 121.2 (2Ar, 12C).

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