



A sustainable approach for synthesizing Diels-Alder adducts using microwave reactor

G. Vinoth Kumar^a, A. Rajendran^{b,*}

^a Research and Development Centre, Bharathiar University, Coimbatore 46, India

^b Department of Chemistry, Sir Theagaraya College, Chennai 21, India



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ABSTRACT

Diels-Alder reactions of 1,3-butadiene, 2,3-dimethyl-1,3-butadiene and 1,3-cyclohexadiene (dienes) with maleic anhydride, maleic acid, 1,4-benzoquinone, 2-cyclopenten-1-one and 2-cyclohexen-1-one (dienophiles) in the presence of 3-methyl-1-octylimidazolium tetrachloroaluminate ionic liquid, namely [C₈MIM] AlCl₄ in conjunction with a variety of solid supports were found to be efficient to afford good to excellent yields both in conventional method at 75 °C and microwave irradiation method at 60 °C. This work-up procedure has many advantages, which include quick reaction, high yields, minimal wastes, recoverability and reusability of ionic liquids and operational simplicity.

1. Introduction

Nowadays pollutants are all around us. The main culprits which are responsible for causing pollution to our mother environment are chemical and pharmaceutical industries as they use huge volume of corrosive solvents. Not only are these solvents health hazards, but they also stick around in the environment if they enter the soil or natural waterways. Once these chemicals get loose into the environment their game on and nasty stuff can happen. Therefore, it is the need of the hour to save our environment from pollution. The easy answer for this is to stop releasing them into the environment. The "green chemistry" movement is gaining huge momentum, largely due to increased awareness of the need to reduce pollution. Both new and old industrial processes are being evaluated and examined to try and reduce and even eliminate negative contributions to the environment (Kunkes et al., 2008; Dodds and Gross, 2007; Huber and Corma, 2007; Chheda et al., 2007; Huber et al., 2006). Many efforts have been taken for the past more than two decades for the development of conducting chemical reactions in alternative reaction media instead of using volatile organic solvents for the reconstruction of a pollutionless environment.

Ionic liquids are eco-friendly chemicals which have been used as an alternative reaction media in the field of synthetic organic chemistry in order to obtain excellent yields in short reaction time. Unlike conventional solvents, ionic liquids play a dual role as solvent as well as catalyst. They have special characteristics to dissolve a majority of organic compounds and could be recycled and reused in subsequent runs without much loss in their efficiency (Anastas, 2011; Lucas et al., 2012).

Classical conventional methods of synthesizing organic compounds devour reaction time in hours or even days. Utilizing microwave technology instead of using classical heating methods which use fire as heating source reduces the reaction times from days to hours or minutes or even seconds. Generally, rate enhancements are attained through thermal/kinetic effect. This effect can be rapidly achieved by microwave irradiation on polar ionic liquid media (Kappe, 2004; Vidis et al., 2008). During the process of microwave irradiation on reaction mixture mediated by ionic liquid, the microwave energy is transferred to substances through dipole rotation and mechanism of ionic conduction leading to enhancement of reaction rates remarkably (Martinez-Palou, 2007). However, it should be noted that microwave energy cannot initiate the chemical reaction as its energy is not sufficient (0.0016 eV) to break the chemical bonds of molecules (Stuerga and Delmotte, 2002; Mingos, 2004; Baghurst and Mingos, 1991; Gabriel et al., 1998). Numerous microwave assisted chemical reactions (Varma and Nambodiri, 2001; Leadbeater and Torenius, 2002; Mayo et al., 2002; Vallin et al., 2002; Martinez-Palou, 2010) including Diels-Alder reactions (Martinez-Palou, 2007; Van der Eycken et al., 2002) have already been performed in ionic liquids under solvent free conditions (Loupy et al., 2004). Mineral supports have also been contributing significantly for the enhancement of the reaction rates of number of ionic liquid mediated Diels-Alder reactions and other conventional reactions considerably (Van der Eycken et al., 2002; Reiser, 1994; Stefaniak et al., 2011; Janus et al., 2010; Bittner et al., 2011; Janus and Bittner, 2010; Janus and Stefaniak, 2008; Silvero et al., 2005; Song et al., 2001; Sarma and Kumar, 2008). Recyclability of these versatile efficient media can

* Corresponding author.

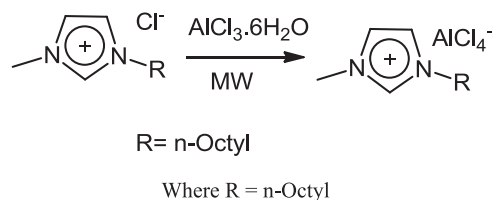
E-mail address: annamalai_rajendran2000@yahoo.com (A. Rajendran).

be reused several times without considerable loss of its activity which in turn make these processes more economic (Bittner et al., 2011; Janus and Stefaniak, 2008; Reinhardt et al., 2008; Nino et al., 2011; Doherty et al., 2007). The tendency of recycling ionic liquids is sufficient considerably to fulfil the Green Chemistry goals of minimization of waste and reduction of energy requirements (Warner oxford press) (Anastas and Warner, 1998).

Conventional Diels-Alder cycloaddition reactions have already been executed in many organic solvents. However, these reactions suffer from serious drawbacks like environmental pollution, high temperature, high pressure and longer duration of hours or even days for the completion of reactions (Kappe, 2004; Vidis et al., 2008). The combined effect of microwave technology and ionic liquids in organic reactions make them overcome these issues. Microwave-assisted and ionic liquid mediated Diels-Alder reactions provide excellent yields than conventional reactions using volatile organic solvents. Particularly, Diels-Alder reactions assisted by imidazolium based ionic liquid have been proved as an ideal combination to enhance the reaction rates enormously (Vidis et al., 2008; 2008, 2005; Sarma and Kumar, 2008; Doherty et al., 2007; Kumar, 2001; Hagiwara et al., 2010; Harifi-Mood et al., 2008; Vidis et al., 2005; Park et al., 2004; Tiwari and Kumar, 2006; Rosa et al., 2011; Bortolini et al., 2010; Acevedo, 2009; Yadav et al., 2003; Yadav et al., 2005; 2003, 2005, 2006; Meracz and Oh, 2003; Yadav et al., 2006; Yin et al., 2005). Herein, we have chosen tetrachloroaluminate ion as negative counter part of the imidazolium ionic liquid. This is because, when an ionic liquid has tetrachloroaluminate ion instead of halide/tetrafluoroborate ion as the negative ion, it achieves better catalytic property in order to give excellent yields in shorter span of reaction time. From the extensive literature survey, it is clearly understood that a number of organic reactions including Michael addition, Diels-Alder reactions, Friedel-Craft reactions, Heck reactions etc., have already been performed exploiting the use of microwave technology and imidazolium based ionic liquid as green medium (Martinez-Palou, 2007). As a part of our ongoing research on ionic liquid mediated Diels-Alder reactions, we investigate herein the coupled effect of solid supports and ionic liquid through conventional and microwave irradiation methods for Diels-Alder reactions involving 1,3-butadiene, 2,3-dimethyl-1,3-butadiene and 1,3-cyclohexadiene as dienes.

2. Materials and methods

Melting and boiling points were determined on a ThermoCal / μ ThermoCal₁₀ automatic capillary point apparatus. All reagents and solid supports were purchased from Sigma-Aldrich. Microwave reactions were performed in a Biotage (Power range: 0–300 W at 2.45 MHz) microwave reactor at 60 °C. Conventional reactions were conducted in a calibrated magnetic stirrer (Remi). All reactions were monitored by a GC-MS spectrometer. Yields refer to isolation of product by solvent extraction using diethyl ether. Evaporation of solvents was carried out at reduced pressure on a Buchi rotary evaporator. ¹H and ¹³C NMR spectra of samples in CDCl₃ were measured on Bruker UxNMR FT-300 MHz (Avance) spectrometers. Chemical shifts of NMR spectra are given in ppm (δ) from the internal TMS standard ($\delta = 0.00$ ppm). GC-MS spectra were recorded on a Thermo LCQ Deca XP MAX GC-MS spectrometer. UV-Visible absorption spectra were measured on a Perkin Elmer, Lambda 35 (USA) UVPC spectrophotometer using a 1 cm (10 mm) quartz cuvette, concentration: 0.0001 mmol mL⁻¹ (Acetone) in the range 190–1100 nm. FT-IR spectra were recorded on a Perkin Elmer, RXI, USA spectrophotometer using a 1 cm (10 mm) quartz cell, concentration: 0.5 mmol mL⁻¹ (Acetone). The Biotage microwave reactor (300 W) was used for the synthesis of ionic liquid.



Scheme 1. Preparation of ionic liquid [C₈MIM] AlCl₄.

2.1. Synthetic procedures

2.1.1. General procedure for the synthesis of ionic liquid

The ionic liquid, 3-methyl-1-octylimidazolium tetrachloroaluminate, [C₈MIM] AlCl₄ was prepared (Scheme 1) from 3-methyl-1-octylimidazolium chloride and aluminiumchloride hexahydrate using the microwave reactor (Biotage, 300 W) in accordance with the procedure given in the literature (Rajendran and Vinoth Kumar, 2016). (Scheme 1)

2.1.2. Spectral data of ionic liquid

¹H NMR (300 MHz, D₂O, ppm, δ) of [C₈MIM] AlCl₄: 0.73(t, J = 3.3 Hz, 2.7 Hz, 3 H, N(CH₂)₇CH₃), 1.13(m, 10 H, N(CH₂)₂(CH₂)₅CH₃), 3.78(s, 3 H, NCH₃), 3.79(s, 2 H, 2NCH), 4.11(m, 2 H, CH₂CH₂(CH₂)₅CH₃), 7.37(t, J = 12.6 Hz, 10.5 Hz, 2 H, NCH₂(CH₂)₆CH₃), 8.62(s, 1 H, N₂CH).

2.1.3. General procedure for the synthesis of the Diels-Alder adducts of 2,3-dimethyl-1,3-butadiene and 1,3-cyclohexadiene by conventional method

Appropriate amount (0.05–1.00 g) of solid support was mixed with 2 mL of [C₈MIM]AlCl₄ ionic liquid in a 25 mL round bottomed vial. After closing the vial, the reaction medium was subjected to homogenization by stirring it well for 30 s. Then, 2.2 mmol of 1, 3-cyclohexadiene and 2 mmol of corresponding dienophile were dissolved in the reaction medium. After closing the vial, the reaction mixture was stirred well in a calibrated magnetic stirrer (Remi) for a given time (Table 1, Table 2 and Fig. 1). The course of the reaction was monitored *in situ* by GC-MS spectrometer. The reaction product was detached out by solvent extraction using diethyl ether (5 × 6 mL). The extracted ethereal solution was concentrated by reducing it to half the volume using a rotary evaporator. The impurity of ionic liquid was eliminated from the organic solution by filtering it using a silica gel bed (3 cm). The organic solvent was completely removed by keeping the extracted solution in a thermostat at 60 °C for 3 h. The yellow liquid was further

Table 1

Comparative study of the reactions between 1,3-cyclohexadiene and the dienophiles namely, 2-cyclopenten-1-one (4) and maleic acid (2) in conventional and microwave methods using various solid supports.

Entry	Dienophile	Solid support ^a	Conventional ^b		Microwave ^c	
			Time, h	Yield ^d , %	Time, min	Yield ^d , %
1	4	LiNTf ₂	0.15	98	0.20	97
2	4	Sc(OTf) ₃	0.30	96	0.20	97
3	4	Y(OTf) ₃	1.15	93	0.20	95
4	4	K-10	1.45	88	0.20	90
5	4	SiO ₂ -60	2.15	85	0.20	88
6	4	Al ₂ O ₃	3.00	82	0.20	86
7	2	LiNTf ₂	1.30	99	2.00	95
8	2	Sc(OTf) ₃	2.00	95	2.00	93
9	2	Y(OTf) ₃	3.15	93	2.00	92
10	2	K-10	4.00	90	2.00	80
11	2	SiO ₂ -60	4.45	88	2.00	78
12	2	Al ₂ O ₃	7.30	87	2.00	76

^a Amount of solid support = 0.750 g.

^b Temperature = 75 °C.

^c Temperature = 60 °C.

^d Isolated yield.

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