

Eco-Friendly Microwave-Assisted Diels-Alder reactions in Ionic Liquid Influenced by Minerals

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Introduction

Room temperature ionic liquids (RTILs), particularly 1,3-dialkyl substituted imidazolium based ionic liquids have been most popularly employed as efficient green catalytic medium in most of the synthetic organic processes. The main advantages of using ionic liquids instead of using hazardous volatile organic solvents in organic synthesis are environmentally friendly nature, recyclability of reaction medium, faster rate of product formation, simple work-up procedure and avoiding or reducing the generation of wastes which causes environmental pollution. Recently, special attention has been paid on microwave reactors for synthesizing organic compounds as the applications of microwave dielectric heating on chemical reactions make the reactions processes smoother and faster. Hence, this present paper focuses efficiency on the use of microwave irradiation in the ionic liquid mediated Diels-Alder reactions.

In the present work, chemo selective Diels-Alder reactions of 1,3-cyclohexadiene with maleic anhydride and 1,4-benzoquinone in an ionic liquid, 3-methyl-1-octyl imidazolium tetrachloroaluminate, [MOIM]AlCl₄ have been reported by both conventional and microwave irradiation methods in the presence of efficient solid supports.

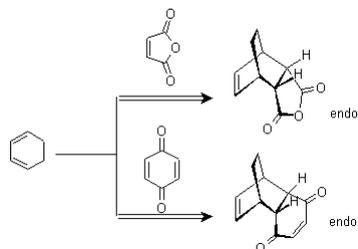


Figure 1. Diels-Alder reactions of 1,3-cyclohexadiene with maleic anhydride and 1,4-benzoquinone.

Methods

The synthesis of (1*R*,6*S*)-4-oxatricyclo[5.2.2.0^{2,6}]undec-8-ene-3,5-dione and (1*R*,7*S*)-tricyclo[6.2.2.0^{2,7}]dodeca-4,9-diene-3,6-dione were performed by conventional magnetic stirring and microwave irradiation methods. All the Diels-Alder reactions were carried out in 2 mL of [MOIM]AlCl₄ at 25°C in conventional method and at 60°C in microwave irradiation method on a Biotage microwave reactor (Power range: 0-300 W at 2.45 MHz) with closed reaction mw-vial of 20 mL. All the reactions were examined by Gas Chromatography-Mass Spectrometer (GCMS Bruker, 45X-GC 44, MS-SCION MS). ¹H and ¹³C NMR spectra were measured on a Bruker 300 MHz instrument (Bruker Avance). UV-Visible absorption spectra were recorded on a Lab India UV-VIS Spectrophotometer 3002. IR spectral measurements were recorded on an FT-IR spectrophotometer (Perkin Elmer, Spectrum RX I, USA) using a 1 cm (10 mm) quartz cell, concentration: 0.5 mmol mL⁻¹. All commercially accessible chemicals were used without further refinements.

Discussion

Diels-Alder reactions of 1,3-cyclohexadiene with maleic anhydride and 1,4-benzoquinone were successfully carried out. In all the experiments, only *endo* adducts were obtained. Spectroscopic measurements revealed a fact that no any *exo* adducts were traced. Figure 4 displays the yields of the solid mineral supported Diels-Alder conventional and microwave assisted reactions of 1,3-cyclohexadiene with maleic anhydride and 1,4-benzoquinone respectively using various solid supports. The efficiency of solid supports, bis(trifluoromethane)sulfonamide lithium (LINT2)(a), scandium trifluoromethanesulfonate, Sc(OTf)₃ (b), yttrium trifluoromethanesulfonate Y(OTf)₃ (c), montmorillonite (K-10) (d), silica gel (SiO₂-60) (e) and alumina (Al₂O₃) (f) were examined

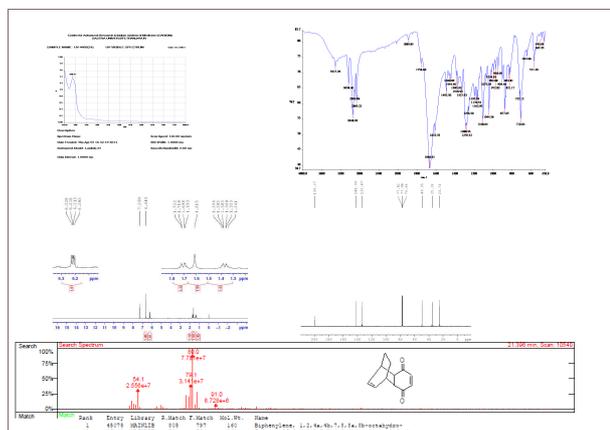


Figure 3. Spectral data of (1*R*,7*S*)-tricyclo[6.2.2.0^{2,7}]dodeca-4,9-diene-3,6-dione (UV-Visible, FT-IR, ¹H-NMR, ¹³C-NMR and GC-MS spectra).

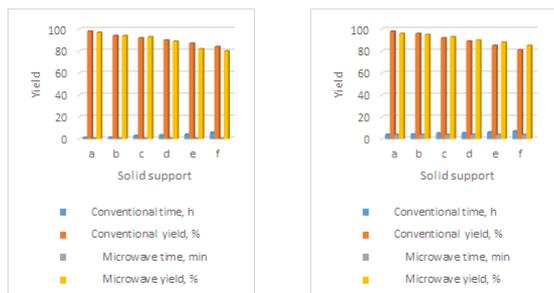


Figure 4. Solid supported, conventional and microwave assisted Diels-Alder reactions of 1,3-cyclohexadiene with i) maleic anhydride ii) 1,4-benzoquinone respectively.

by adding 0.750 g of solid support to 2 mL of the ionic liquid. For the dienophile maleic anhydride, conventional reactions completed in the range of 1.15 - 6.00 h and microwave reactions completed in 45 s and for 1,4-benzoquinone, conventional reactions completed in 4.00 - 7.15 h and microwave reactions at a fixed time of 4 min. It suggests that maleic anhydride acts as an effective dienophile in Diels-Alder reactions. Figure 4 shows that LINT2 (a) is an excellent and efficient solid support rather than others chosen in this investigation. Moreover, it reveals that the Diels-Alder reactions of 1,3-cyclohexadiene with maleic anhydride take place more rapidly than with that of 1,4-benzoquinone.

Figure 5 shows the optimum efficiency of LINT2 while using 0.750/1.000 g of this mineral in various load study of this mineral. Figure 6 depicts the efficiency of the ionic liquid (after recycling) in terms of yield and rate. It reveals that the ionic liquid [MOIM]AlCl₄ can be used for the reactions for at least five times without appreciable loss of activity. In all the experiments, the products were analysed by ¹H, ¹³C, UV-Visible, FTIR and GCMS spectroscopic techniques.

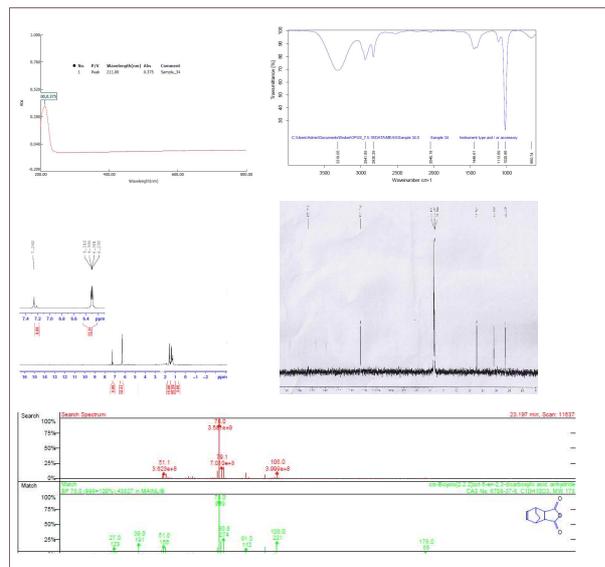


Figure 2. Spectral data of (1*R*,6*S*)-4-oxatricyclo[5.2.2.0^{2,6}]undec-8-ene-3,5-dione (UV-Visible, FT-IR, ¹H-NMR, ¹³C-NMR and GC-MS spectra).

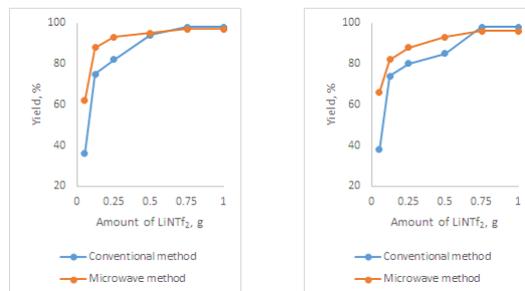


Figure 5. LINT2 load study of conventional and microwave assisted Diels-Alder reactions of 1,3-cyclohexadiene with i) maleic anhydride ii) 1,4-benzoquinone respectively.

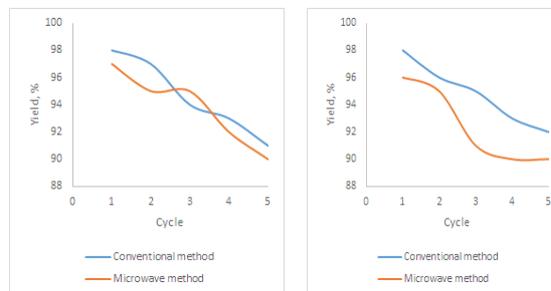


Figure 6. Recycle study of ionic liquid mixed with 0.750 g of LINT2 for the Diels-Alder reaction of 1,3-cyclohexadiene with i) maleic anhydride and ii) 1,4-benzoquinone respectively.

Conclusion

The Diels-Alder adducts of 1,3-cyclohexadiene were obtained only as *endo*. The rates of the Diels-Alder reactions were measured as a function of efficiency of both ionic liquid and solid supports. While the ionic liquid facilitates the organic reactions in a rapid manner rather than the reactions of conventional volatile organic solvents, its effectiveness is further enhanced by the addition of right quantity of suitable solid support (LINT2). In both the conventional and microwave methods, the solid supports, LINT2, Sc(OTf)₃, Y(OTf)₃ showed significant activity.

Acknowledgements

The supports and appreciations of Bharathiar University, Coimbatore and Sir Theagaraya College, Chennai, India are gratefully acknowledged.