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Remarkable Rate Acceleration of Microwave-Assisted Diels-Alder Reaction in Recyclable Novel Imidazolium Ionic Liquid Supported by Minerals

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ABSTRACT

Microwave-assisted synthesis of 3-methyl-1-octyl-imidazolium tetrachloroaluminate, [MOIM] $AlCl_4$ and its application as recyclable media in Diels-Alder reaction between isoprene and maleic anhydride are described. This manuscript analyses the efficiency of inorganic minerals as solid supports for enhancing rates of Diels-Alder reaction.

1. Introduction

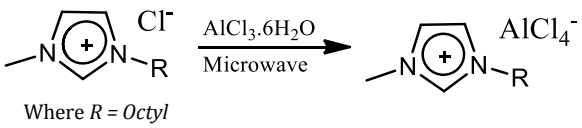
Ionic liquids known as dipolar aprotic solvents [1] are widely used as green medium in most of the Diels-Alder reactions, Friedel-Crafts alkylation and Heck reactions [2-6]. In recent years, the room temperature ionic liquids have occupied a significant part in catalysis [7-9], separation process [10], and preparation of organic compounds [11-12] by using as unique solvents. These ionic liquids have many advantages over conventional organic solvents in the view of environmental pollution, catalytic activity [2, 4, 13-16] and recycling process [17].

Imidazolium based tetrachloroaluminate ionic liquids are behaving as very active catalyst than tetrafluoroborate ionic liquids for conventional and microwave assisted organic reactions [18]. In recent years, solid supports have been widely used to improve the catalytic activity of ionic liquids [17-19]. These tetrachloroaluminate ionic liquids behave not only as a good medium for Diels-Alder reactions but also catalysts for enhancing reaction rates [20]. Ionic liquids are considered as a potential solvents as their miscibility nature with a number of organic and inorganic compounds giving rise to homogeneous phase of the resulting mixture [4]. Recently, room temperature ionic liquids have occupied impressive position in organic synthesis as their nature of non-volatility, non-flammability, high dissolving capacity and easy way of recycling process. Because of its non-volatile nature, they can be used in high-vacuum conditions as reaction media [6, 21]. The first green mediated Diels-Alder reaction was reported for the first time by Jaeger, followed by a number of reporters [22-25]. In recent years, several imidazolium ionic liquids mediated Diels-Alder reactions have been reported [23, 26-28]. Because of the influence nature of Lewis acids on the rate of Diels-Alder reaction, chloroaluminate ionic liquids are used widely [29-32]. Microwave-assisted synthesis is a novel technology for synthesizing organic compounds by reducing reaction time and improving yields of reactions [2, 4, 13-16]. Although the exact cause of impact of ionic liquids on reaction rates was not well known, high internal solvent pressure [33], hydrogen bonding [24-25], polarity of solvents [34] and Lewis acidity [35] are considered as the reasons for its catalytic properties. From literature, it is known that most of the ionic liquids have high decomposition temperatures [36]. Moreover, the green mediated Diels-Alder reactions have no considerable vapour pressure, are non-explosive and thermally stable [26].

This manuscript covers the syntheses of Diels-Alder adduct using the synergistic combination of [MOIM] $AlCl_4$ ionic liquid and microwave irradiation supported by minerals.

2. Experimental Methods

The melting point was measured using a ThermoCal / μThermoCal$_{10}$ automatic capillary point apparatus. Ionic liquid [MOIM] $AlCl_4$ was prepared (Scheme 1) utilizing IFB household microwave oven (700 Watts) according to the procedure described in the literature [37]. A LCMS instrument (Thermo LCQ Deca XP MAX) equipped with electrospray (ESI) and APCI ionization (positive or negative mode) sources was used to monitor the course of all the reactions. IR spectra were recorded on an FT-IR spectrophotometer (Perkin Elmer, Spectrum RX I, USA) having 1 cm (10 mm) quartz cell. Progress of the reactions were analyzed by ^{1}H and ^{13}C NMR spectra, recorded on a Bruker 300 MHz instrument (300.13 MHz). UV-Visible absorption measurements were performed on a Perkin Elmer, Lambda 35 (USA) UVPC spectrophotometer using a 1 cm (10 mm) quartz cuvette. A microwave synthesizer (Biotage, Power range: 0-300 W at 2.45 MHz) was utilized for all the microwave-assisted Diels-Alder reactions to be carried out.



Scheme 1. Preparation of ionic liquid [MOIM] $AlCl_4$.

2.1 General procedure for the conventional synthesis of 5-methyl-3a,4,7,7a-tetrahydro-2-benzofuran-1,3-dione

A mixture of isoprene **1** (2.2 mmol), maleic anhydride **2** (2 mmol) (Fig. 6) and 0.750 g of corresponding solid support were taken in a round bottomed flask of 25 mL capacity containing 2 mL of [MOIM] $AlCl_4$. The reaction mixture was subjected to magnetic stirring at room temperature for an appropriate time as indicated in Table 1. The progress of the reaction was monitored by LCMS instrument. The reaction mixture was then extracted with diethyl ether (6 × 5 mL) and successively poured into a 100 mL beaker. The ethereal solution was evaporated to half the volume

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under reduced pressure and then filtered through a 3 cm silica gel bed, to liberate any ionic liquid contamination. The solution was then evaporated to dryness and if necessary, was purified by recrystallization using n-hexane to give excellent yield of **a** (Fig. 6). The final product was analyzed by ^{1}H, ^{13}C NMR, IR, UV-Vis and LCMS measurements.

2.2 General procedure for the microwave synthesis of 5-methyl-3a,4,7,7a-tetrahydro-2-benzofuran-1,3-dione

A mixture of isoprene **1** (2.2 mmol), maleic anhydride **2** (2 mmol) and 0.750 g of corresponding solid support were taken in a mw-vial equipped with magnetic stirrer of 20 mL capacity containing 2 mL of [MOIM] $AlCl_4$. The vial was adopted into the Biotage Initiator plus microwave synthesis system and heated to 60 °C for one minute with 15 seconds of initial mixing. The progress of the reaction was monitored by LCMS instrument. The resulting mixture was extracted and purified as stated above (Section 2.1). Finally, the product was analyzed by ^{1}H, ^{13}C NMR, IR, UV-Vis and LCMS.

*2.3 General procedure of crystallization of solid product **a***

The Diels-Alder adduct was mixed with hot n-hexane solvent in an Erlenmeyer flask and then swirled to dissolve the solid. The flask was placed on a steam bath to keep the solution warm. When the solid was all in solution, the flask was kept on the bench top without disturbing it. After appearing crystals, the flask was placed in an ice bath to complete the crystallization process. Then it was dried through vacuum filtration.

2.4 Spectral Data of Diels-Alder adduct (Fig.1-5)

*5-methyl-3a,4,7,7a-tetrahydro-2-benzofuran-1,3-dione (**a**):*

Crystalline colourless solid, MP: 65°C.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.48 (3H, s, $-CH_3$), 2.12 (1H, m, $-CH_2$), 2.26 (1H, dd, $-CH_2$), 2.71 (1H, m, -CHCO), 4.15 (1H, t, $=CH_2$).
^{13}C NMR (300 MHz, Acetone-d_6): δ 23.62, 26.91, 36.78, 39.67, 40.39, 120.09, 133.20, 206.56.
LCMS (m/z) (R. Time 7.66-7.93) + ESI: $[M+H]^+$ = 167.33, 162.20, 157.33, 148.33, 145.33, 131.27, 79.20, 74.20.
(R. Time 4.95-7.08 min) + ESI: $[M+H]^+$ = 167.0, 161.33, 157.27, 153.40, 148.33, 131.33, 101.27, 79.20.
(R. Time 4.82-7.20 min) - ESI: $[M+H]^+$ = 167.27, 147.20, 129.20, 115.20, 113.27, 71.13.
IR (KBr): 925, 1260, 1800, 1700, 1385, 1740, 2980, 2890, cm^{-1}.
UV/Vis λ_{max} ($CDCl_3$) nm: 360.91.

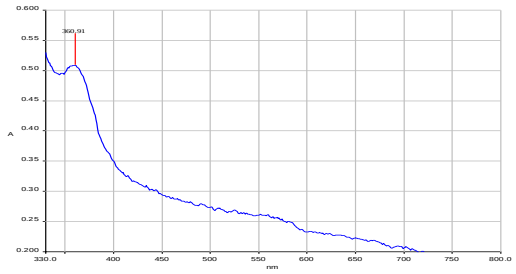

Fig. 1 UV-Visible spectrum of **a**.

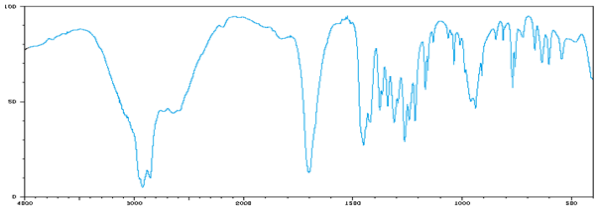

Fig. 2 IR spectrum of **a**.

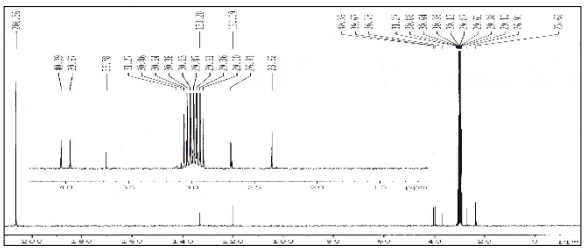

Fig. 3 ^{13}C NMR spectrum of **a**

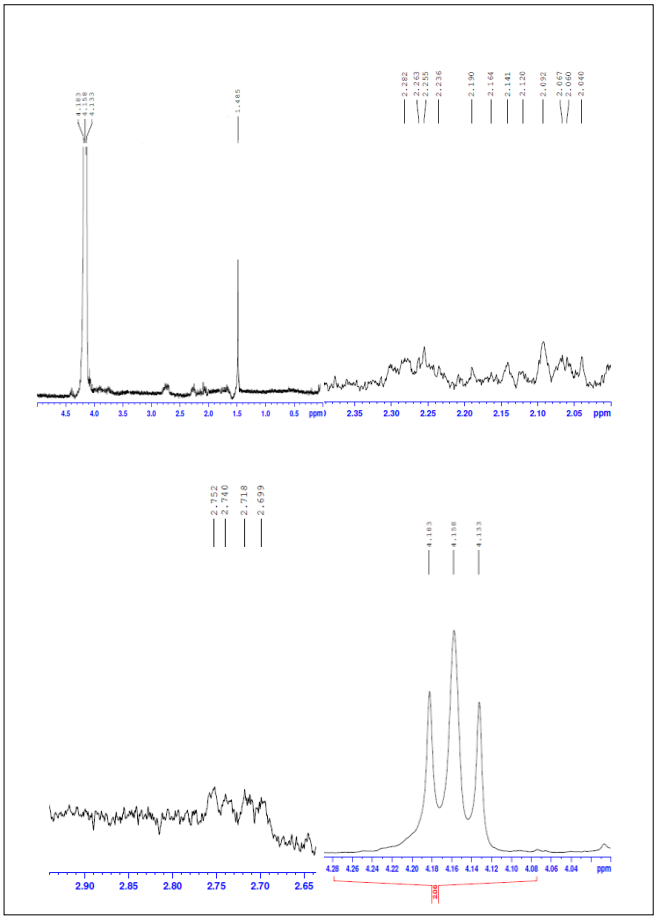

Fig. 4 ^{1}H NMR spectrum of **a**

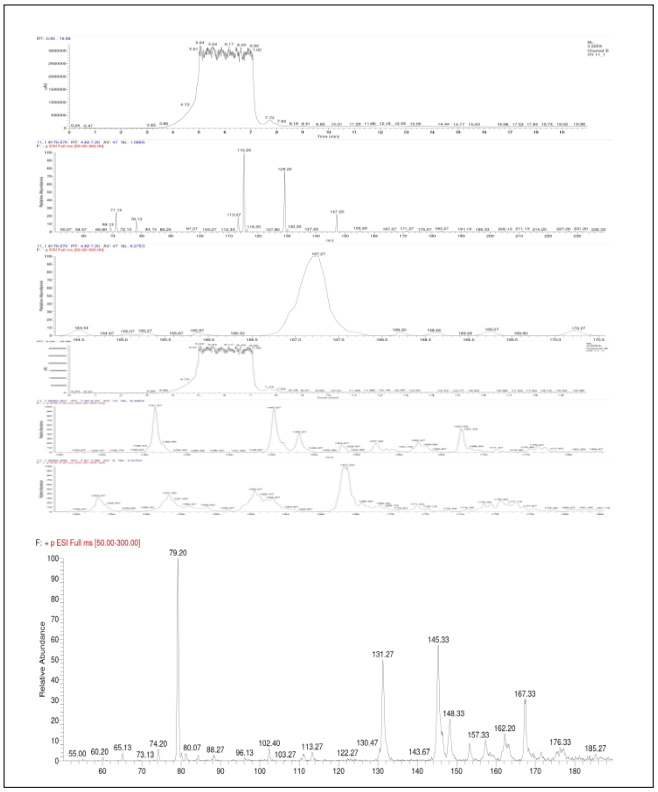

Fig. 5 LCMS spectrum of **a**.

3. Results and Discussion

Herein, we report a developed methodology for the synthesis of 5-methyl-3a,4,7,7a-tetrahydro-2-benzofuran-1,3-dione (**a**) (Fig. 6) in [MOIM] $AlCl_4$ mixed with solid support by both microwave irradiation and conventional methods.

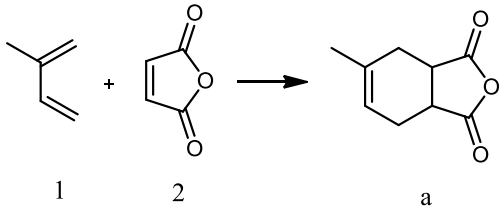

Fig. 6 Diels-Alder reaction between isoprene and maleic anhydride

Table 1 Comparative study in terms of yield (Diels-Alder adduct **a**) and reaction period for microwave and conventional techniques using various solid supports.

Entry	Soild support[a]	Conventional[b]		Microwave[c]	
		Time (h)	Yield (%) [d]	Time (min)	Yield (%) [e]
1	$LiNTf_2$	1.30	98	1.00	98
2	$Sc(OTf)_3$	2.00	96	1.00	96
3	$Y(OTf)_3$	3.15	94	1.00	93
4	K-10	4.00	93	1.00	90
5	SiO_2-60	4.45	91	1.00	83
6	Al_2O_3	7.00	88	1.00	81

Reaction conditions: [a]amount of solid support = 0.750 g, [b] performed at room temperature, 2 mL of [MOIM] $AlCl_4$. [c] temperature= 60 ℃, microwave, 2mL of [MOIM] $AlCl_4$. [d,e] Isolated yield.

Table 2 Comparative study in terms of yield (Diels-Alder adduct **a**) and reaction period for microwave and conventional techniques using $LiNTf_2$.

Entry	Amount of $LiNTf_2$ (g)	Conventional[a]		Microwave[b]	
		Time (h)	Yield (%) [c]	Time (min)	Yield (%) [d]
1	0.050	1.30	43	1.00	65
2	0.125	1.30	82	1.00	90
3	0.250	1.30	89	1.00	92
4	0.500	1.30	94	1.00	96
5	0.750	1.30	98	1.00	98
6	1.000	1.30	98	1.00	98

Reaction conditions: [a] performed at room temperature, 2 mL of [MOIM] $AlCl_4$, [b] temperature= 60 ℃, microwave, 2 mL of [MOIM] $AlCl_4$, [c,d] Isolated yield.

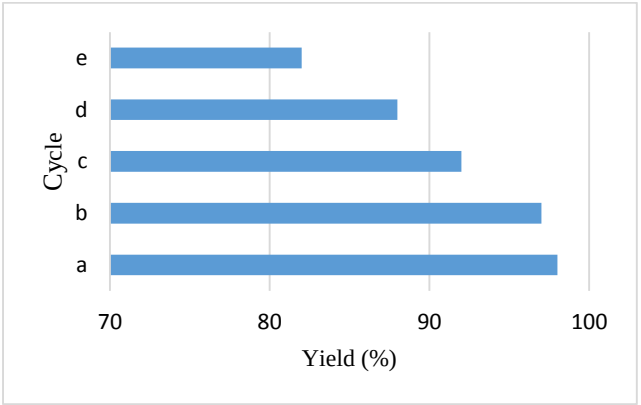

Fig. 7 Recyclability of the system, ionic liquid [MOIM] $AlCl_4$ plus $LiNTf_2$ for the reaction between isoprene and maleic anhydride in conventional method. (*Reaction conditions: 2 mL of [MOIM] $AlCl_4$, 0.750 g of $LiNTf_2$, performed at room temperature, isolated yield, time = 1.30 h)*

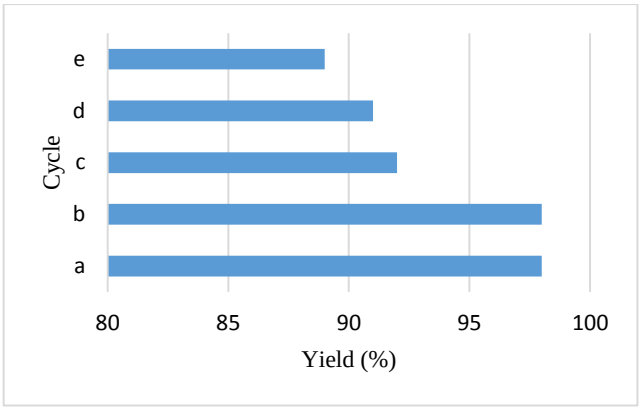

Fig. 8 Recyclability of the system, ionic liquid [MOIM] $AlCl_4$ plus $LiNTf_2$ for the reaction between isoprene and maleic anhydride under mw irradiation. *(Reaction conditions: 2 mL of [MOIM] $AlCl_4$, 0.750g $LiNTf_2$, temperature= 60 ℃, microwave, isolated yield, time = 1.00 min)*

In order to obtain high yield, a group of solid supports were selected for the reaction between isoprene and maleic anhydride because of their efficiency in the green mediated reactions [17]. The selected solid supports are bis(trifluoromethane)sulfonimide lithium ($LiNTf_2$), scandium trifluoromethanesulfonate, $Sc(OTf)_3$, yttrium trifluoromethanesulfonate $Y(OTf)_3$, montmorillonite (K-10), silica gel (SiO_2-60) and alumina (Al_2O_3). In this present experiment, 0.750 g of solid support was used for each reaction (Table 1). The maximum reaction rate was observed when the ionic liquid [MOIM] $AlCl_4$ was mixed 0.750 g of $LiNTf_2$ (entry 1) comparing to the other solid supports in both conventional and microwave irradiation techniques. Among the six number of solid supports aluminium oxide showed the least activity (entry 6) in both the techniques. However there was a significant improvement in the reaction rate of microwave irradiation techniques. While the conventional reactions took hours of duration for the completion of reactions microwave tests finish within 1 min. The order of reactivity for both the techniques was in the order $LiNTf_2$> $Sc(OTf)_3$> $Y(OTf)_3$> K-10 > SiO_2-60 > Al_2O_3.

Because of the better efficiency of $LiNTf_2$ (Table 1), its activity was further analyzed by varying the amount of $LiNTf_2$ in the range of 0.050-1.00 g (Table 2) using microwave and conventional methods. It should be noted that there was good conversion rate observed in both the techniques when 0.750 g/1.0 g of solid support was used (entry 5 & 6). Particularly it should be indicated that the minimum dosage of 0.750 g of $LiNTf_2$ is sufficient to give excellent yields in both conventional and microwave techniques (entry 5) instead of using 1.00 g of $LiNTf_2$. There was a remarkable increase in the yield observed while changing the amount of $LiNTf_2$ from 0.050 to 0.125 g.

In green chemistry, the reuse of catalyst and solvent are seriously recommended. Before recycling, the ionic liquid was purified under vacuum at 75 °C for 2 h and the purity was confirmed by ^1H NMR [38]. Therefore, the best combination, i.e., 0.750 g plus 2 mL of [MOIM] $AlCl_4$ was subjected to recycling process until the completion fifth duplicate reaction (Fig. 7). In this graphical representation, it is observed that there is almost equal and highest reaction rates for first two cycles in both conventional and microwave techniques (Fig. 7 and Fig. 8). But in conventional technique there is a gradual and slight decrease in the rate of the reaction from cycle 3 to 5. For microwave recycled reactions the rate of reactions were not much distinguished among cycle 3 to 5 (Fig. 8) like the same case of Fig. 7. It means that the activity of green medium in microwave synthesis was not lost as much as in the case of conventional method during the course of the reactions using recycled ionic liquid. All the microwave tests (1.30 h, Fig. 7) and conventional reactions (1.00 min, Fig. 8) were conducted by keeping constant time. Finally, it should be noted that the progress of all the microwave assisted Diels-Alder reactions completed within a minute while conventional magnetic stirring methods proceed by hours of duration.

4. Conclusion

Our study has shown for the first time [MOIM] $AlCl_4$ ionic liquid can be used efficiently both as solvent and catalyst in the Diels-Alder reaction. The solid supports and microwave irradiation have occupied a significant role in the rate enhancement. Applications of this novel green medium are under investigation in our laboratory for other reactions.

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References

[1] S.N.V.K. Aki, J.F. Brennecke, A. Samanta, How polar are room-temperature ionic liquids?, Chem. Commun. 5 (2001) 413-414.
[2] R. Sheldon, Catalytic reactions in ionic liquids, Chem. Commun. 23 (2001) 2399-2407.
[3] P. Wasserscheid, W. Keim, Ionic Liquids—New "Solutions" for transition metal catalysis, Angew. Chem. Int. Ed. 39(21) (2000) 3772-3789.
[4] T. Welton, Room-temperature ionic liquids. Solvents for Synthesis and Catalysis, Chem. Rev. 99(8) (1999) 2071-2084.
[5] M.J. Earle, K.R. Seddon, Ionic liquids: Green solvents for the future, Pure Appl. Chem. 72(7) (2000) 1391-1398.
[6] A. Kumar, Salt Effects on Diels-Alder reaction, Kinetics Chem. Rev. 101(1) (2001) 1-19.
[7] V.I. Parvulescu, C. Hardacre, Catalysis in ionic liquids, Chem. Rev. 107(6) (2007) 2615-2665.
[8] F. Van Rantwijk, R.A. Sheldon, Biocatalysis in ionic liquids, Chem. Rev. 107(6) (2007) 2757-2785.
[9] T. Welton, Ionic liquids in catalysis, Coord. Chem. Rev. 248(21-24) (2004) 2459-2477.
[10] X. Han, D.W. Armstrong, Ionic liquids in separations, Acc. Chem. Res. 40(11) (2007) 1079-1086.
[11] M. Haumann, A. Riisager, Hydroformylation in room temperature ionic liquids (RTILs): catalyst and process developments, Chem. Rev. 108(4) (2008) 1474-1497.
[12] Z.C. Zhang, Catalysis in ionic liquids, Adv. Catal. 49 (2006) 153-237.
[13] R. Martinez-Palou, Microwave-assisted synthesis using ionic liquids, Mol. Divers 14(1) (2010) 3-25.
[14] C.C. Tzschucke, C. Markert, W. Bannwarth, S. Roller, A. Hebel, R. Haag, Modern separation techniques for the efficient workup in organic synthesis, Angew. Chem. Int. Ed. 41(21) (2002) 3964-4000.
[15] M. Gordon, New developments in catalysis using ionic liquids, Appl. Catal., A 222 (2001) 101-117.
[16] K.R. Seddon, Room-temperature ionic liquids—neoteric solvents for clean catalysis, Kinet. Catal. 37(5) (1996) 693-697.
[17] I. Lopez, G. Silvero, M.J. Arevalo, R. Babiano, J.C. Palacious, J.L. Bravo, Enhanced Diels–Alder reactions: on the role of mineral catalysts and microwave irradiation in ionic liquids as recyclable media, Tetrahedron, 63(13) (2007) 2901-2906.
[18] R. Martinez-Palou, Ionic liquid and microwave-assisted organic synthesis: a "Green" and synergic couple, J. Mex. Chem. Soc. 51(4) (2007) 252-264.
[19] C.E. Song, M.Y. Yoon, D.S. Choi, Significant improvement of catalytic efficiencies in ionic liquids, Bull. Korean Chem. Soc. 26(9) (2005) 1321-1330.
[20] A. Kumar, S.S. Pawar, Converting exo-selective Diels–Alder reaction to endo-selective in chloroaluminate ionic liquids, J. Org. Chem. 69(4) (2004) 1419-1420.
[21] G.F. Vafina, R.R. Fazlyev, F.Z. Galin, L.V. Spirikhin, Ionic liquid-catalyzed Diels-Alder reaction of levopimaric acid with quinones. Russ. J. Org. Chem. 45(4) (2009) 500-504.
[22] D.A. Jaeger, C.E. Tucker, Diels-Alder reactions in ethylammonium nitrate, a low-melting fused salt, Tetrahedron Lett. 30(14) (1989) 1785-1788.
[23] T. Fischer, A.R. Sethi, T. Welton, J. Woolf, Diels-Alder reactions in room-temperature ionic liquids, Tetrahedron Lett. 40(4) (1999) 793-796.
[24] A. Aggarwal, N.L. Lancaster, A.R. Sethi, T. Welton, The role of hydrogen bonding in controlling the selectivity of Diels–Alder reactions in room-temperature ionic liquids, Green Chem. 4(5) (2002) 517-520.
[25] A. Vidis, C.A. Ohlin, G. Laurenczy, E. Kusters, G. Sedelmeier, P.J. Dyson, Rationalisation of solvent effects in the Diels-Alder reaction between cyclopentadiene and methyl acrylate in room temperature ionic liquids, Adv. Synth. Catal. 347(2-3) (2005) 266-274.
[26] M.J. Earle, P.B. McCormac, K.R. Seddon, Diels-Alder reactions in ionic liquids: A safe recyclable green alternative to lithium perchlorate-diethyl ether mixtures, Green Chem. 1(1) (1999) 23-25.
[27] P. Ludley, N. Karodia, Phosphonium tosylates as solvents for the Diels–Alder reaction, Tetrahedron Lett. 42(10) (2001) 2011-2014.
[28] S. V. Dzyuba, R.A. Bartsch, Expanding the polarity range of ionic liquids, Tetrahedron Lett. 43(26) (2002) 4657-4659.
[29] M.A. Forman, W.P. Dailey, The lithium perchlorate-diethyl ether rate acceleration of the Diels-Alder reaction: Lewis acid catalysis by lithium ion, J. Am. Chem. Soc. 113(7) (1991) 2761-2762.
[30] G. Desimoni, G. Faita, P. P. Righetti, Lithium perchlorate catalysis of the hetero Diels-Alder reaction: a specific lithium cation effect, Tetrahedron 47(39) (1991) 8399-8406.
[31] R.M. Pagni, G.W. Kabalka, S. Bains, S. Plesco, J. Wilson, J. Bartmess, A chemical, spectroscopic, and theoretical assessment of the Lewis acidity of lithium perchlorate in diethyl ether, J. Org. Chem. 58(11) (1993) 3130-3133.
[32] G. Springer, C. Elam, A. Edwards, C. Bowe, D. Boyles, J. J. Bartmess, et al., Chemical and spectroscopic studies related to the Lewis acidity of lithium perchlorate in diethyl ether, J. Org. Chem. 64(7) (1999) 2202-2210.
[33] R.V. Eldik, T. Asano, W.J. Le Noble, Activation and reaction volumes in solution, Chem. Rev. 89(3) (1989) 549-688.
[34] J.A. Berson, Z. Hamlet, W.A. Mueller, The Correlation of solvent effects on the stereoselectivities of Diels-Alder reactions by means of linear free energy relationships. A new empirical measure of solvent polarity, J. Am. Chem. Soc. 84(2) (1962) 297-304.
[35] S. Otto, W. Blokzijl, J.B.F.N. Engberts, Diels-Alder reactions in water. Effects of hydrophobicity and hydrogen bonding, J. Org. Chem. 59(18) (1994) 5372-5376.
[36] P. Bonhote, A.P. Dias, N. Papageorgiou, K. Kalyanasundaram, M. Gratzel, Hydrophobic, Highly conductive ambient-temperature molten salts, Inorg. Chem. 35(5) (1996) 1168-1178.
[37] V.V. Namboodiri, R.S. Varma, Microwave-assisted preparation of dialkylimidazolium tetrachloroaluminates and their use as catalysts in the solvent-free tetrahydropyranylation of alcohols and phenols, Chem. Commun., (4) (2002) 342-343.
[38] F. Zulfiqar, T. Kitazume, One-pot aza-Diels-Alder reactions in ionic liquids. Green Chem. 2(5) (2000) 137-139.