



Diels-Alder reactions in green medium by microwave irradiation supported by bis (trifluoromethane) sulfonimide lithium

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ABSTRACT

The present work explores in detail the combined effect of solid support bis (trifluoromethane) sulfonamide lithium (LiNTf₂) and microwave (MW) irradiation in green medium, 3-methyl-1-octyl-imidazolium tetrachloroaluminate [MOIM] AlCl₄ on Diels-Alder reactions between isoprene and a series of dienophiles. Reactions have been carried out with and without solid support and by both conventional and MW assisted techniques, and a detailed comparison is made.

Key words: Diels-Alder reaction, Ionic liquid, 3-methyl-1-octyl-imidazolium tetrachloroaluminate AlCl₄, Microwaves, Solid support.

1. INTRODUCTION

Diels-Alder reaction is an important protocol for the synthesis of simple and complex cyclic carbo- or heterocyclics which are otherwise ubiquitous in natural products. Conventional Diels-Alder reactions suffer from certain practical difficulties like poor yield, kinetically slower rate, less purity of the main product and so on [1]. The main theme of this research work is to synthesize certain substituted cyclic compounds through Diels-Alder reactions without the aforementioned practical difficulties. To overcome such practical difficulties, green chemistry methods are being used. A very recent trend in the development of environmentally benign processes is to use room temperature ionic liquids (RTILs) for Diels-Alder reactions. Conventional Diels-Alder reaction used for the synthesis of homo and heterocyclic organic compounds accompany large number of varieties of the reaction medium, catalysts, and favorable reaction conditions to enhance reaction rates which ultimately cause environmental degradation [2].

For accelerating reaction rates, so many novel efforts have been made using Lewis acid catalysts [3-5], solid-support catalysts [6,7], applying favorable pressure, and temperature conditions [8-10], using ultrasound in chemical reactions [11,12] and microwave (MW) irradiation [13-17]. To explore the reactivity of mineral supports scandium triflate [18], bis (trifluoromethane) sulphonamide lithium and other solid supports [19] have

been used. Nowadays, RTILs have attained a significant role for synthesizing organic compounds which occur in a scheduled time [20-27]. In recent days, MW reactors play a vital role using MW irradiation to facilitate the organic synthesis [28-31]. Using MW reactors, we can easily pre-set and monitor the reaction conditions such as temperature and time [2,31]. Organic reactions exploiting ionic liquids coupled with MW are carried out effectively through ionic conduction mechanism with the advantages of high heating rate and extremely low pressure [17,30-37].

MW assisted organic synthesis is considered as an extremely powerful technology. Dielectric heating, i.e. heating by MW irradiation, has many advantages from conductive heating because it involves core heating by direct interaction of reactants and/or solvents with the MW electromagnetic field. As a result, scheduled reaction temperatures can be reached in minutes or even seconds, which usually translates in cleaner and faster reactions [38]. RTILs are known as green solvents as [27,39,40] (a) they have extremely low vapor pressure, (b) they play dual role as solvent and catalyst, (c) they possess high thermal stability (c) they can be recovered and reused for subsequent runs. The main objective of the present work is twofold. The first one is to carry out the Diels-Alder reactions with and without using solid support and by conventional and MW assisted techniques with a view to ascertain the cumulative

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efficiency of LiNTf₂, ionic liquid 3-methyl-1-octyl-imidazolium tetrachloroaluminate [MOIM] AlCl₄ and MW. Moreover, the second objective is to recover the ionic liquid for the recycling process. In this paper, syntheses of Diels-alder adduct 1a-1e (Figure 1) using [MOIM] AlCl₄ have been reported.

2. EXPERIMENTAL

2.1. Materials and Measurements

Ionic liquid [MOIM] AlCl₄ was synthesized from IFB household MW reactor (700 Watts) using the procedure described in the literature [41]. Isoprene, Maleic anhydride, Maleic acid, 1,4-benzoquinone, 2-cyclohexene-1-one, 2-cyclopentene-1-one, LiNTf₂ and [MOIM] Cl were purchased from Aldrich Chemical Company Inc. and used as received. All other reagents were of analytical grade.

2.2. Physical Techniques

All melting and boiling points were determined on a ThermoCal/μ ThermoCal₁₀ automatic capillary point apparatus. Infrared (IR) spectra were recorded in the range 4000-400 cm⁻¹ on an Fourier transform-IR spectrophotometer (Perkin Elmer, Spectrum RX I, USA) using a 1cm (10 mm) quartz cell, concentration: 0.5 mmol mL⁻¹ (Acetone). Solid samples were recorded on KBr (Merck) pellets and, liquid samples as a film between NaCl plates (Spectra Tech). ¹H and ¹³C nuclear magnetic resonance (NMR) spectra were measured on a Bruker 300 MHz instrument (300.13 MHz). Chemical shifts are given in ppm

(δ) from the internal tetramethylsilane standard (δ=0.00 ppm). Absorption spectra were scanned on a UVPC absorption spectrophotometer (Perkin Elmer, Lambda 35, USA) using a 1 cm (10 mm) quartz cuvette, concentration: 0.0001 mmol mL⁻¹ (Acetone) in the range 190 nm-1100 nm. GC-MS spectra were obtained from a Thermo LCQ Deca XP MAX GC - MS instrument equipped with electrospray ionization (ESI) and atmospheric pressure chemical ionization (positive or negative mode) sources. LC-MS spectra were also recorded on a Thermo LCQ Deca XP MAX LC-MS instrument. Acetone (99.5% purity) and chloroform (99.5% purity) (Alfa-Aesar, UK) were used at high-performance liquid chromatography grade. All MW tests were carried out on a Biotage MW reactor (power range: 0-300 W at 2.45 MHz) at 60°C. For all experiments in this paper, results correspond to, at least duplicate runs. Work-up consisted of the extraction of the products from the reaction media with diethyl ether and further purification by crystallization if necessary.

All reactions were monitored by GCMS/LCMS spectrometer (Thermo LCQ Deca XP MAX) and/or ¹H NMR spectrometer.

2.3. Preparation of ionic liquid

The ionic liquid, [MOIM] Cl purchased from Sigma-Aldrich was dried, and the purity was checked by recording ¹H NMR spectrum. The ionic liquid, [MOIM] AlCl₄ was synthesized by the standard procedure reported in the literature [41]. An IFB household MW oven (17PM-MEC1) with 700 W of maximum power output was used for this experiment. MW heating provides an efficient way in attaining and controlling in a particular temperature range and gives the highest yield of product so rapidly in contrast to the normal conventional heating techniques. A reaction mixture of 20 mmol of [MOIM] Cl and 20 mmol of aluminum chloride hexahydrate (AlCl₃.6H₂O) were mixed using a vortex mixer and heated (30 s × 7 times, 360 W) in the IFB MW oven (scheme 1), which was reported by Nambodiri and Varma [41]. The final product was a clear homogenized phase in contrast to the heterogeneous phases of the reactants. All the ionic liquids used in this study were systematically dried by heating at 70°C under vacuum for 5 days. The purity of the final product was confirmed by recording ¹H NMR. The product was a colorless liquid with a yield of 100%. ¹H NMR (D₂O): δ 0.72 (3H,t,N(CH₂)₇CH₃), 1.13(10H,m,N(CH₂)₂(CH₂)₅CH₃), 3.78 (3H,s,NCH₃), 3.82 (2H,t,NCH₂(CH₂)₆CH₃), 4.11 (2H,m,CH₂CH₂(CH₂)₅CH₃), 0.37 (2H,s,2NCH), 8.62(1H,s,N₂CH).

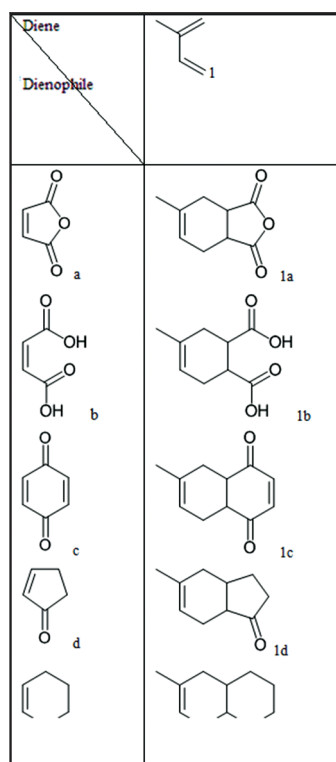
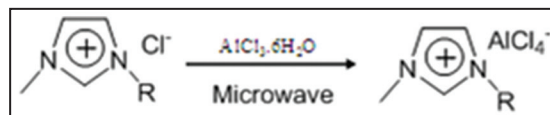


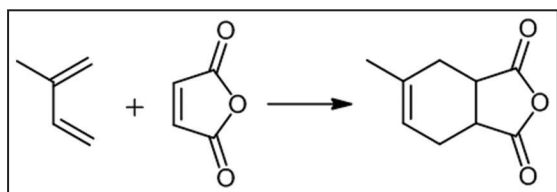
Figure 1: The numbering scheme for the dienes, Dienophiles, and the Diels-Alder adducts.



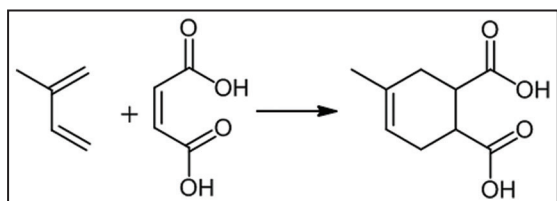
Scheme 1: Preparation of [MOIM] AlCl₄ using MW irradiation, Where R= Octyl

2.4. Representative procedure for cycloaddition reactions with and without solid supports in conventional method (Schemes 2-6)

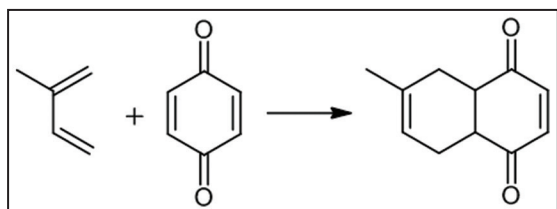
In a round-bottomed vial of 25 ml capacity containing 2 ml of [MOIM] AlCl₄ ionic liquid and, if applicable, 0.750 g of LiNTf₂, 2.2 mmol of isoprene 1 and 2.0 mmol of dienophile were added under stirring at room temperature. All procedures were monitored by ¹H NMR and/or GCMS/LCMS. After completion or scheduled time, whichever applicable, the crude



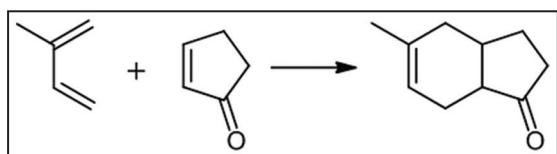
Scheme 2: Synthesis of 1a.



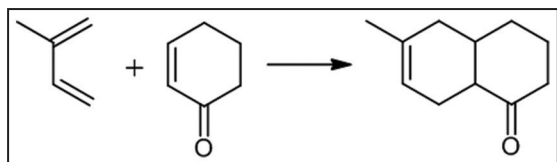
Scheme 3: Synthesis of 1b.



Scheme 4: Synthesis of 1c.



Scheme 5: Synthesis of 1d.



Scheme 6: Synthesis of 1e.

Reaction conditions: (a) performed at room temperature, [OMIM] AlCl₄. (b) temperature=60°C, microwave, [OMIM] AlCl₄. (c) performed at room temperature, [OMIM] AlCl₄, 0.750g of LiNTf₂. (d) temperature=60°C, microwave, [OMIM] AlCl₄, 0.750g of LiNTf₂

was extracted with diethyl ether (6 ml × 5 ml) and subsequently decanted off. The ethereal solution was reduced to half volume under vacuum in a rotary evaporator and then filtered through a 3 cm silica gel bed, to avoid contamination of the ionic liquid. The final adducts were isolated by evaporation of the crude mixture and, if necessary, purified by crystallization. Finally, it was analyzed by ¹H, ¹³C NMR, IR, UV-Vis, and GCMS/LCMS.

2.5. Representative Procedure for MW Irradiated Cyclo Addition Reactions

Isoprene 1 (2.2 mmol) and the dienophile (2 mmol) were dissolved in [MOIM] AlCl₄ (2 mL) and, if applicable, mixed and homogenized with 0.750 g of LiNTf₂, in a 20 mL MW-vial equipped with a magnetic stirring bar. The resulting solution was heated to 60°C (0 bar) on Biotage Initiator plus MW synthesis system for a programmed time. The resulting solution was cooled to room temperature and extracted, purified using previously described procedure (Section 2.4). Finally, it was analyzed by ¹H, ¹³C NMR, IR, UV-Vis, and GCMS/LCMS.

2.6. Representative procedure of crystallization of solid products 1(a), 1(b) and 1(c)

The solid adduct to be recrystallized was placed in an Erlenmeyer flask. The boiled and hot n-hexane solvent was poured into the flask containing the solid substance. The flask was swirled to dissolve the solid. The flask was placed on a steam bath to keep the solution warm. After some time, the crystals appeared. Then the flask was placed in an ice bath to complete the crystallization process. Then it was dried through vacuum filtration.

2.7. Spectral Data of Diels-Alder adducts

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

Crystalline colorless solid, MP: 65°C. ¹H NMR (300 MHz, CDCl₃): δ 1.48 (3H, s, -CH₃), 2.12 (1H, m, -CH₂), 2.26 (1H, dd, -CH₂), 2.71 (1H, m, -CHCO), 4.15 (1H, t, =CH₂).

¹³C NMR (300 MHz, Acetone-d₆): δ 23.62, 26.91, 36.78, 39.67, 40.39, 120.09, 133.20, 206.56.

LCMS (m/z) (Running Time 7.66-7.93) + ESI: [M+H]⁺ = 167.33, 162.20, 157.33, 148.33, 145.33, 131.27, 79.20, 74.20.

(Running Time 4.95-7.08) + ESI: [M+H]⁺ = 167.0, 161.33, 157.27, 153.40, 148.33, 131.33, 101.27, 79.20.

(Running Time 4.82-7.20) - 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} (CDCl₃) nm: 360.91.

(b) 4-methylcyclohex-4-ene-1,2-dicarboxylic acid (1b):

Crystalline colorless solid, MP: 120°C. ¹H NMR (300 MHz, Acetone-d₆): δ 1.88 (3H, s, -CH₃),

2.00 (1H, m, -CH₂, merged with acetone peak), 2.18(1H, m, -CH₂), 2.64 (1H, dd, -CH₂), 2.85 (1H, m, -CHCO), 4.15 (1H, dd, =CH), 4.56 (1H, m, -CHCO), 10.006 (2H, s, 2 -COOH).

¹³C NMR (300 MHz, CDCl₃): δ 13.18, 19.31, 31.89, 36.31, 49.93, 117.64, 136.05, 182.45.

GCMS (m/z) (Running Time 18.858). +ESI: [M+H]⁺ = 184.9, 179.0, 173.0, 160.8, 155.9, 147.8, 139.1, 132.9, 127.9, 123.1, 117.0, 109.1, 101.1.

IR (KBr): 3555.39, 3159.18, 1718.57, 1574.73, 1464.50, cm⁻¹.

UV/Vis λ_{max} (Acetone-d₆) nm: 246.37.

- (c) 1,4-Naphthoquinone,4a,5,8,8a-tetrahydro-6-methyl (1c):

Crystalline dark Brown solid, MP: 78°C. ¹H NMR (300 MHz, dimethyl sulfoxide [DMSO]-d₆): δ 1.76 (3H, s, -CH₃), 2.48 (1H, dd, -CH₂, merged with DMSO peak), 2.26 (1H, dd, -CH₂, merged with DMSO peak), 3.22 (1H, m, -CH, merged with HOD peak of DMSO), 3.386 (1H, m, -CH, merged with HOD peak of DMSO), 3.6 (2H, dd, -CH₂, merged with HOD peak of DMSO), 4.138 (1H, t, -CH), 7.762 (1H, s, -CH), 7.769 (1H, s, -CH).

¹³C NMR (300 MHz, Acetone-d₆): δ 23.993, 32.934, 36.546, 42.146, 46.426, 60.372, 126.390, 133.234, 217.026 (merged with solvent acetone).

GCMS (m/z) (Running Time 17.06) +ESI: [M]⁺ = 176.5175, 161.4628, 147.5357, 143.5381, 134.5358, 131.5000, 120.4895, 115.4695, 110.4445, 105.4458, 98.3966, 91.4622, 77.4005, 74.3842, 65.5971, 58.1174.

(Running Time 17.49) +ESI: [M]⁺ = 176.6211, 161.5675, 149.2303, 131.5099, 115.4648, 104.4174, 93.4352, 76.3913,

IR (KBr): 3325.17, 2927.62, 2852.17, 1736.21, 1363.44, cm⁻¹.

UV/Vis λ_{max} (Acetone-d₆) nm: 340.98.

- (d) 5-methyl-2,3,3a,4,7,7a-hexahydro-1H-inden-1-one (1d):

Yellow liquid, BP: 232°C. ¹H-NMR (300 MHz, CDCl₃): δ 1.67 (3H, s, -CH₃), 2.15 (1H, m, -CH₂), 2.20 (1H, m, -CH₂), 2.70 (1H, m, -CH), 2.76 (1H, td, -CH), 4.85 (1H, m, -CH₂), 5.10 (1H, t, =CH), 5.76 (1H, dd, -CH₂).

¹³C- NMR (300 MHz, CDCl₃): δ 22.468, 26.019, 28.723, 29.583, 31.545, 36.227, 50.151, 122.217, 135.927, 217.003.

GCMS (m/z) (Running Time 18.714) + ESI: [M]⁺ = 150.0, 144.0, 139.1, 132.0, 127.0, 122.0, 113.1, 104.0.

IR (NaCl): 3437.50, 1629.85, 1599.51, 1360.79, 744.14, cm⁻¹.

UV/Vis λ_{max} (CDCl₃) nm: 250.48.

- (e) 6-methyl-3,4,4a,5,8,8a-hexahydronaphthalen-1(2H)-one (1e)

Yellow liquid, BP: 251°C. ¹H NMR (300 MHz, CDCl₃): δ 1.40 (2H, m, -CH₂), 1.66 (3H, s, -CH₃), 1.86 (2H, m, -CH₂), 2.41 (2H, dd, -CH₂), 2.33 (2H,

t, -CH₂CO), 4.20 (2H, m, -CH₂).

¹³C NMR (300 MHz, CDCl₃): δ 11.87, 18.09, 21.60, 29.24, 30.69, 34.95, 48.42, 116.68, 134.98, 207.62.

GCMS (m/z) (Running time 18.702 min) +ESI: [M]⁺ = 164.0, 162.0, 149.0, 132.0, 122.0, 112.1, 104.0.

IR (NaCl): 3459.28, 2830.54, 2725.33, 1630.11, 1354.88, 743.82, cm⁻¹.

UV/Vis λ_{max} (CDCl₃) nm: 256.83.

2.8. Method of Percentage of Yield Calculation

$$\% \text{ of Yield} = \frac{\text{Actual mass (g) of adduct}}{\text{Expected mass (g) of adduct}} \times 100$$

Expected mass = Mass of 2 mmol of isoprene + Mass of 2 mmol of dienophile. (or) mass of 2 mmol of the Diels-Alder adduct.

3. RESULTS AND DISCUSSION

The main aim of our experiment was to explore the best results when ionic liquid [MOIM] AlCl₄ is coupled with MW irradiation or solid support (LiNTf₂) or with both of these combinations in Diels-Alder reactions. We used LiNTf₂ as solid support due to its best enhancing capability of the reaction rates [19]. It should be noted that the ionic liquid, [MOIM] AlCl₄ was used both as solvent and catalyst for the first time in the history of Diels-Alder reactions. The two main advantages of using tetrachloroaluminate ionic liquids are (a) They are not explosive like ethyl ammonium nitrate and (b) Unlike water; most organic molecules are soluble in RTILs [42]. This means that reactions can be performed at synthetically useful scales in chloroaluminate ionic liquids. Diels-Alder reactions of isoprene 1 with five dienophiles namely maleic anhydride a, maleic acid b, 1, 4-benzoquinonec, 2-cyclopentene-1-one d, 2-cyclohexene-1-one were carried out by both conventional and MW irradiation methods to obtain the Diels-Alder adducts 1a, 1b, 1c, 1d and 1e respectively (Figure 2).

The reasons for the selection of [MOIM] AlCl₄ are (a) it can be synthesized in a straightforward manner (b) the reaction products can be easily extracted with diethyl ether (c) it is relatively cheaper for synthesis. (d) It does not interact with the behavior of Lewis acid catalysts due to its neutral and weakly coordinating nature.

Diels-Alder reactions of isoprene with chosen dienophiles proceeded in this ionic liquid at 25°C in conventional magnetic stirring method and at 60°C in MW reactor (Table 1). At these reaction conditions, several hours of time for conventional reactions, but only a few minutes in the range of 6-20 min was needed to obtain high yields of product

for the reactions conducted in MW reactor. Among these five reactions, the reaction between isoprene 1 and 2-cyclopentene -1-one d took place rapidly in both conventional and MW heating methods while 1, 4-benzoquinone c, and isoprene 1 combination took longer duration for the reaction to complete. Comparing the reactivity of d and e, the dienophile 2-cyclopentene -1-one d has the better tendency to act as a dienophile toward the diene 1 although they have same functional group. Likewise, it was observed that the activity of the anhydride dienophile 1a has the better activity than 1b in all the reactions.

In our work, all the reactions were carried out by both conventional and MW irradiation methods using 0.750 g of LiNTf₂ (Table 2) also. It should be noted that rates of the reactions were enhanced remarkably compared to the reactions without solid support. Entry 3 in Table 2 shows slowest reaction rate in both conventional and MW heating methods while entry 4 shows the highest reaction rates for the dienophile d. From this fact, we come to know that LiNTf₂ affected the Diels-Alder reaction positively, by enhancing yields rather than what previously observed from Table 1 for these set of duplicate reactions.

The comparison of reaction rates of dienophiles a-e with isoprene 1 in conventional method has given as a graphical representation (Figure 3). This figure shows the highest conversion rate of these reactions while using 0.750 g of LiNTf₂. For all the reactions of this set, conversion time was reduced from several hours to few minutes or few hours.

Table 1: Tests of diene 1 without solid support.

Entry	Dienophile	Conventional ^a time, h	Yield ^c (%)	Microwave ^b time, min	Yield ^d (%)
1	a	10.00	90	10.00	96
2	b	14.00	90	17.00	93
3	c	20.00	82	20.00	95
4	d	08.00	92	06.00	93
5	e	15.00	98	18.00	91

Reaction conditions: ^aperformed at room temperature, [OMIM] AlCl₄. ^btemperature=60°C, microwave, [OMIM] AlCl₄. ^{c,d}Isolated yield

Table 2: Tests of diene 1 with solid support.

Entry	Dienophile	Conventional ^a time, h	Yield (%)	Microwave ^b time, min	Yield (%)
1	a	1.30	98	1.00	98
2	b	2.00	97	3.00	97
3	c	5.30	98	5.00	97
4	d	0.30	99	0.15	97
5	e	3.00	98	3.30	98

Reaction conditions: ^aperformed at room temperature, [OMIM] AlCl₄, 0.750g of LiNTf₂. ^btemperature=60°C, microwave, [OMIM] AlCl₄, 0.750g of LiNTf₂. ^{c,d}Isolated yield

When these reactions were carried out using MW reactor, all the reactions were almost completed

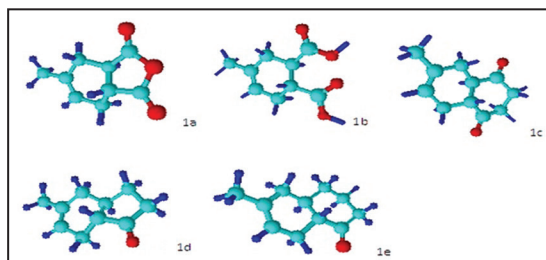


Figure 2: 3-D models of diels-alder adduct 1a, 1b, 1c, 1d, and 1e, respectively.

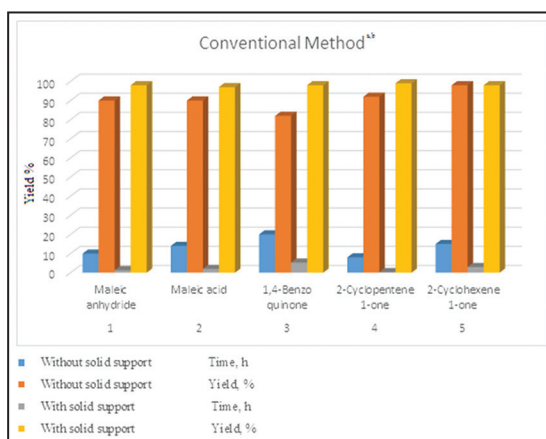


Figure 3: Graphical representation of Diels-Alder reaction of 1 with dienophiles, Reaction conditions:^aperformed at room temperature, [OMIM] AlCl₄, ^bperformed at room temperature, [OMIM] AlCl₄, 0.750g of LiNTf₂

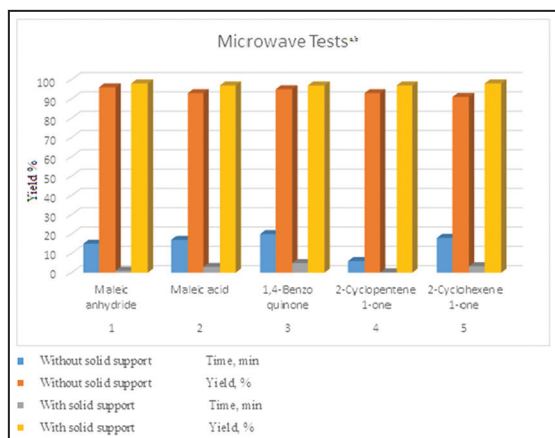


Figure 4: Graphical representation of Diels-Alder reaction of 1 with Dienophiles,^atemperature= 60°C, microwave, [OMIM] AlCl₄.^btemperature= 60°C, microwave, [OMIM] AlCl₄, 0.750g of LiNTf₂.

within few minutes whether using or even not using any mineral support (Figure 4). On the addition of 0.750 g of LiNTf₂ to the ionic liquid, the reaction rates are enhanced from several minutes to few minutes. Simply saying, on the overall analysis, the rate of transformations at given duration was increased remarkably when these green mediated reactions were combined with solid support and MW irradiation.

4. CONCLUSION

In summary, the inorganic solid support, known as LiNTf₂, in combination with ionic liquids has been used for enhancing the rates of Diels-Alder reactions enormously. It has proved that this protocol stands as an efficient methodology in improving reaction rates. We have proved that the method of ionic liquid coupled with MW irradiation provides good rate enhancement for the completion of Diels-Alder reaction which occurs comparatively so rapidly. Under the given set of reaction conditions, no decomposition of tetrachloroaluminate was observed. These methodologies will be helpful in future for the other organic reactions in a modified and improved way to occur.

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