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Synthesis of [RMIM] Acetate Halogen-Free Ionic Liquids for Use as Greener Solvents in Diels-Alder Reaction

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A halogen-free ionic liquid 1-alkyl-3-methylimidazolium acetate, [RMIM]OAc, with its cation based on 1-alkyl-3-methyl imidazolium and with the halogen-free anion acetate (OAc) was synthesized. This ionic liquid's distinctive solvent properties and its application as greener solvent for the Diels-Alder reaction were examined. Its efficiency as medium for the Diels-Alder reaction between cyclopentadiene and methyl acrylate was evaluated in terms of product yield and stereoselectivity. Using these parameters, [RMIM]OAc was compared with other solvents such as benzene, methanol, and water as alternative solvent for the Diels-Alder reaction. Results showed a decrease in product yield as the length of the alkyl group chain on the imidazolium cation is increased from C_6 to C_{12}. In terms of stereoselectivity, there is a general preference for the *endo*-product in all of the solvents tested. The endo-selectivity obtained with [HMIM] OAc (endo:exo=91:9) is remarkably high and is more desirable compared to that obtained with water (endo:exo=76:24).

Key Words: Diels-Alder reaction, Hydrogen-bonding, Imidazolium, Ionic Liquids, Stereoselectivity

INTRODUCTION

The development of cleaner technologies is a major emphasis in green chemistry. Among the several features of green chemistry, the reduction/replacement of volatile organic compounds (VOCs) from the reaction medium is of greatest concern. VOCs have been heavily implicated in causing changes to the global climate, the formulation of smog, as well as being identified as a source of ozone depletion (Holbrey and Seddon 1999). Based on the large quantities of volatile compounds lost or consumed, replacement with greener, less polluting and non-volatile alternatives will permit significant advances towards pollution control. Ionic liquids (ILs) are a class of solvents that can be used as alternative reaction media.

In general, ILs consist of a salt where one or both ions are large, and the cation has a low degree of symmetry. These properties tend to reduce the lattice energy of the crystalline form of the salt, hence lowering the melting point which usually occurs below 100°C (Seddon 1998). The low melting point of ILs make these useful as solvents in many reactions and because the ILs are made of ions rather than molecules, a number of reactions namely Lewis and Bronsted Acid catalysis, metal-mediated C-C bond formation, hydrogenation, hydroformylation and oxidation, performed in such medium as compared to conventional organic solvents proceed with a higher selectivity and rate (Welton 1999; Olivier-Bourbigou and Magna 2002; Clarke et al. 2004). Ionic liquids come in two main categories, namely simple salts (made of a single cation and anion) and binary ionic liquids (salts where equilibrium is involved). Examples of ILs consisting of a simple salt are shown in Figure 1. Many of these materials have an imidazolium based cation. By changing the anion and the alkyl chain on the cation moiety, a wide

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variation of properties such as hydrophobicity, viscosity, density, and solvation can be obtained. In the liquid state, the individual ions can move freely around and interact, and easily dissolve chemicals added to the reaction flask, the solubility being controlled by the nature of the counter anion (Koel 2000).

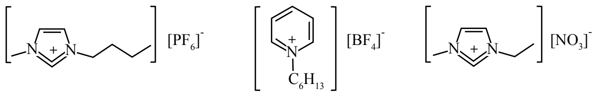

Figure 1. Examples of simple ionic liquids.

Ionic liquids have been demonstrated to be effective solvents for the Diels-Alder reactions (Jaeger and Tucker 1989; Earl et al. 1998; Fisher et al. 1999) and show significant rate enhancements, high yields, and selectivity comparable with the best results obtained in conventional solvents. These show that the IL-based Diels-Alder reaction is more efficient than its organic solvent-based counterpart. This is further demonstrated by the ease of product separation from the IL reaction mixture: the product floats to the top of the reaction vessel and can be skimmed off, like cream from milk, so that no complicated work-up is needed to isolate the products. The ionic liquid solvent itself can be reused.

In view of the emerging importance of benign and environment friendly ILs, this study aims to explore the synthesis of a new series of greener ILs based on 1-alkyl-3-methylimidazolium cation with acetate as the halogen-free anion. Acetate anion was chosen because the metabolic pathways it follows in the environment are known (Garett and Grisham 2005) and are apparently environmentally benign. This study also aims to evaluate the application of ILs as greener solvents in the Diels-Alder reaction using cyclopentadiene-methyl acrylate system.

MATERIALS AND METHODS

General Analytical Procedure

The progress of the reaction was monitored by thin layer chromatography. A small amount of the reaction mixture was obtained and applied onto a pre-coated TLC plastic sheet (silica gel 60 F_{254}, Merck) intermittently after which each plate is developed in hexane and subsequently in an iodine chamber to visualize the chromatograms. Normal phase column chromatography with isocratic elution using silica gel 60 (63-200mesh, Merck) was subsequently employed in the purification of the Diels-Alder product. Products were characterized by the usual techniques. FTIR spectra were recorded using BIORAD FTS-40A spectrometer with KBr as reference. Mass spectral analyses were carried out using Finnigan MAT LCQ mass spectrometer. The products were dissolved in HPLC grade methanol or acetonitrile. Nuclear magnetic resonance (NMR) spectra were measured using JEOL Lambda 400 NMR spectrometer.

The solvents used were either HPLC or AR grade. Deionized distilled water was used for the reactions. Reagents were obtained from Fluka: 1-methylimidazole (MIM), alkyl bromides (RBr), and NaOAc were all used as received. Methyl acrylate (Fluka) was distilled prior to use while cyclopentadiene was freshly prepared by thermally cracking dicyclopentadiene (Tedia) at about 210°C and the desired diene collected by distillation at the temperature range 40-45°C.

The stereochemistry (endo:exo ratio) of the product of the Diels-Alder reaction was determined by gas chromatography using SHIMADZU-14B GC-FID with the following parameters: column: J&W Scientific 122-7032 DB-WAX, 30 m, 0.25 mm; carrier gas: N_2; injector temperature:150°C; detector temperature: 200°C; column temperature: 100°C; flow rate: 5mL/min.

Synthetic Procedures

Synthesis of 1-alkyl-3-methylimidazolium bromide [RMIM]Br

Typical Procedure. 1-Bromoalkane (RBr) (20 mmol) with R ranging from C_6 to C_{12} and 1-methylimidazole (20 mmol, 1.59 mL) were stirred thoroughly in a round-bottom flask and heated to 80° C for 48 h or until a clear single phase was obtained. The resulting viscous liquid was cooled to room temperature, washed several times with ethyl acetate (3 x 20 mL) to remove unreacted starting materials and then dried under vacuum at 80°C to afford 1-alkyl-3-methylimidazolium bromide.

1a). [HMIM]Br: 95% yield; IR (film, cm^{-1}):3079, 2937, 2867, 1644, 1566, 1466, 1169; MS [m/z] (relative abundance): $\{[C_{10}H_{19}N_2]^+\}$ 167.23. (100); ^{1}H-NMR (d_6-DMSO): δ (ppm) = 0.704 (t, J = 6.5 Hz, 3H), 1.114 (m, 6H), 1.711 (qnt, J = 6.5 Hz, 2H), 3.888 (s, 3H), 4.212 (t, J = 7.5 Hz, 2H), 7.911 (d, J = 1.5 Hz, 1H), 8.012 (s, J = 1.5 Hz, 1H), 9.613 (s, 1H); ^{13}C-NMR (d_6-DMSO): δ=13.555, 21.680, 24.909, 29.308, 30.364, 35.704, 48.432, 122.055, 123.226, 136.389.

1b). [OMIM]Br: 95% yield; IR (film, cm^{-1}):3085, 2929, 2856, 1578, 1458, 1169; MS [m/z] (relative abundance): $\{[C_{12}H_{23}N_2]^+\}$ 195.29 (100); ^{1}H-NMR (d_6-DMSO): δ (ppm) = 0.728 (t, J = 6.5 Hz, 3H), 1.125 (m, 10H), 1.725 (qnt, J = 6.5 Hz, 2H), 3.889 (s, 3H), 4.215 (t, J = 7.0 Hz, 2H), 7.906 (d, J = 1.5

Hz, 1H), 7.998 (d, J = 1.5 Hz,1H), 9.607 (s, 1H); ^{13}C-NMR (d_6-DMSO): δ=13.635, 21.875, 25.317, 28.226, 28.350, 29.388, 31.002, 35.677, 48.441, 122.064, 123.252, 136.407.

1c). [DMIM]Br: 89% yield; IR (film, cm^{-1}):3153, 3070, 2993, 2848, 1566, 1458, 1173; MS [m/z] (relative abundance): {$[C_{14}H_{27}N_2]^+$} 223.30 (100), 0.732 (t, J = 7.5 Hz, 3H), 1.156 (m, 14H), 1.725 (qnt, J = 7.0 Hz, 2H), 3.893 (s, 3H), 4.216 (t, J = 7.0 Hz, 2H), 7.910 (d, J = 1.5 Hz, 1H), 7.996 (d, J = 2.0 Hz, 1H), 9.608 (s, 1H); ^{13}C-NMR, (d_6-DMSO): δ=13.617, 21.928, 25.352, 28.324, 28.563, 28.758, 28.811, 29.423, 31.144, 35.686, 48.441, 122.055, 123.252, 136.416.

1d). [DDMIM]Br: 88% yield; IR (film, cm^{-1}):3060, 2917, 2852, 1636, 1578, 1181; MS[m/z] (relative abundance): {$[C_{16}H_{31}N_2]^+$} 250.5 (2); ^{1}H-NMR (d_6-DMSO): δ (ppm) = 0.847 (t, J = 6.8 Hz, 3H), 1.266 (m, 18H), 1.852(qnt, J = 6.8 Hz, 2H), 4.102 (s, 3H), 4.288 (t, J = 7.2 Hz, 2H), 7.240 (d, J = 1.4 Hz, 1H), 7.316 (d, J = 2.2 Hz, 1H), 10.451 (s, 1H); ^{13}C-NMR, (d_6-DMSO): δ=13.713, 21.845, 25.392, 28.231, 28.635, 28.127, 28.158, 29.785, 31.156, 35.965, 48.235, 122.045, 123.323, 136.463.

Synthesis of the Halogen-Free Ionic Liquid [RMIM]OAc

Typical Procedure. NaOAc (0.0379 mol) and [RMIM]Br (0.0484 mol) were dissolved in hot water (60°C, 20 mL) in a beaker, then water was slowly removed under vacuum at 70-80°C causing white solids to precipitate out. The solids were filtered and the liquid mixture was transferred to a separatory funnel; CH_2Cl_2 (45 mL) was added to extract the product. The ionic liquid separated into the lower layer, while NaBr was removed in the upper layer. The clear but slightly yellow extract was then washed several times with water (20 mL) and the white solid (NaBr by-product) was separated out. Washing was repeated until IL was bromide-free (2-3 drops of 0.1 M $AgNO_3$ were added to the washings to confirm the presence/absence of bromide ions). The extract was distilled to remove CH_2Cl_2 and was finally dried in vacuum for several hours to afford the corresponding ionic liquid product.

2a). [HMIM]OAc: 81% yield; IR (film, cm^{-1}):3157, 3099, 2937, 2856, 1644, 1578, 1466, 1167; ^{1}H-NMR (d_6-DMSO): δ = 0.814 (t, J = 6.8 Hz, 6H), 1.256 (m, J = 12.8 Hz, 6H), 1.458 (qnt, J = 6.8 Hz, 2H), 1.833 (qnt, J = 6.8 Hz, 2H), 2.338(s. 3H), 4.066 (t, J = 10.4 Hz, 3H), 4.264 (t, J = 7.2 Hz, 2H), 7.365 (d, J = 1.2 Hz, 1H), 7.509 (d, J = 1.6 Hz, 1H), 10.148 (s, 1H); ^{13}C-NMR (d_6-DMSO): 12.619, 20.135, 21.049, 24.520, 28.922, 29.761, 35.437, 48.666, 76.679,121.334, 122.705, 135.534, 171. 485.

2b). [OMIM]OAc: 79% yield; IR (film, cm^{-1}): 3149, 3087, 2929, 2856, 1721, 1570, 1466, 1169; ^{1}H-NMR (d_6-DMSO): δ =0.825 (t, J = 6.4 Hz, 6H), 1.239 (m, 10H), 1.820 (qnt, J = 7.2 Hz, 2H), 2.727(s. 3H), 4.080 (t, J = 10.8 Hz, 3H), 4.272 (t, J = 7.2 Hz, 2H), 7.303 (d, J = 1.2 Hz, 1H), 7.445 (d, J = 1.6 Hz, 1H), 10.289 (s, 1H); ^{13}C-NMR (d_6-DMSO): δ δ 10.716, 19.74, 21.875, 25.317, 28.226, 28.350, 29.388, 31.002, 35.677, 48.441, 122.064, 123.352, 136.391, 171.36.

2c). [DMIM]OAc: 78% yield; IR (film, cm^{-1}):3157, 3083, 2937, 2848, 1721, 1636, 1566, 1466, 1173; ^{1}H-NMR (d_6-DMSO): δ 0.837 (t, J = 6.4 Hz, 6H), 1.212 (m, 14H), 1.836 (qnt, *7.2* Hz, 2H), 2.488 (s, 3H), 4.092 (t, J = 10.8 Hz, 3H), 4.261 (t, J = 7.2 Hz, 2H), 7.236 (d, J = 2.0 Hz, 1H), 7.353 (d, J = 2.0 Hz, 1H), 10.389 (s, 1H); ^{13}C-NMR (d_6-DMSO): δ 13.617, 19.63, 21.928, 25.352, 28.324, 28.563, 28.758, 28.811, 29.423, 31.144, 35.686, 48.441, 122.055, 123.252, 136.416, 171.52.

2d). [DDMIM]OAc: 74% yield; IR (film, cm^{-1}):3164, 3087, 2929, 2848, 1659, 1578, 1466, 1161; ^{1}H-NMR (d_6-DMSO): δ =0.844 (t, J = 6.8 Hz, 3H), 1.260 (m, 18H), 1.800 (qnt, J = 6.8 Hz, 2H), 1.902 (s. 3H), 4.102 (t, J = 10.4 Hz, 3H), 4.306 (t, J = 7.2 Hz, 2H), 7.241 (d, J = 1.2 Hz, 1H), 7.339 (d, J = 1.6 Hz, 1H), 10.448(s, 1H); ^{13}C-NMR (d_6-DMSO): δ 13.713, 19.52, 22.152, 25.738, 28.543, 28.700, 28.8975, 28.963, 29.687, 31.266, 35.965, 49.361, 121.505, 123.505, 135.904, 171.891.

Diels-Alder Reaction: Synthesis of bicyclo-[2.2.1]-hept-5-ene-2-carboxylic acid methyl ester

Methyl acrylate (37.5 mmol, 3.4 mL) and freshly cracked cylcopentadiene (25 mmol, 2.1 mL) were placed in a screw-capped round-bottom flask containing the corresponding IL (12 mmol) or other solvent (5 mL) (H_2O, benzene or methanol) and stirred for six hours at 60°C.

The Diels-Alder product was separated from the reaction mixture by decantation and/or extraction with hexane and purified through column chromatography over silica gel with hexane-ethyl acetate (10:1, v/v) as the mobile phase.

RESULTS AND DISCUSSION

Synthesis of Ionic Liquids

In this study, a new series of greener ILs based on 1-alkyl-3-methylimidazolium cation with acetate (OAc) as the halogen-free anion was synthesized: 1-methylimidazole was reacted with alkyl bromides (R = C_6 , $C_{8,}$ C_{10}, C_{12}) and then the bromide ions were exchanged with OAc to afford the products. The general reaction is presented in Figure 2. The products were purified by extraction with CH_2Cl_2. The solvent was removed by distillation and the final ILs were dried under vacuum. The exchange of Br with the desired anion was evident in the formation of a white precipitate which is presumably NaBr. It was also observed that the apparent viscosity of the ILs increases as the alkyl substituent R on the cation increases in length.

This synthetic route produced good yields of [RMIM]OAc. The products were characterized based on spectroscopic data. The upfield ^{1}H NMR signals (δ=0.76-4.2 pm) for the intermediate products, [RMIM]Br, indicated the successful S_N2 attachment of the alkyl group onto the quaternary N of the imidazolium ring. The highest value is designated to the proton nearest to the electronegative N atom. The downfield peaks (δ=7.8-10.4 ppm) are for the protons in sp^2 carbons of the imidazolium ring. Presence of OAc as the anion produced additional peaks at δ=1.9-2.7 ppm which is due to protons in the acetate group.

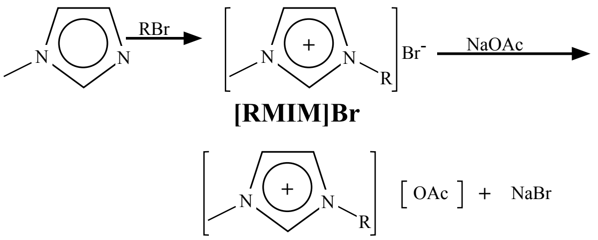

Figure 2. General schematic diagram for the synthesis of [RMIM]OAc.

The ^{13}C NMR-DEPT spectra for [RMIM]Br showed two C upfield (δ=13 and 35 ppm) signals for CH_3 and three C downfield (122, 123, and 136 ppm) signals for CH_2 substituents with the latter peaks concomitantly rising with increasing number of C in the alkyl chain. Results showed 5, 7, 9, and 11 CH_2 peaks for R = C_6, C_8, C_{10} and C_{12}, respectively. The replacement of the bromide with the acetate group produced an additional peak at around 171 ppm which corresponds to the carbonyl C.

FTIR results showed all functional groups expected for the desired ILs. Prominent C=N (1637 cm^{-1}, m), C=C (1575 cm^{-1}, m), and C-N (1172 cm^{-1}, s) peaks verified the presence of an imidazolium ring while C-O (1217 cm^{-1}, b), and C=O (1721 cm^{-1}, s) verified that the anion is acetate. An intense and broad band signal for -OH group (3460 cm^{-1}) was also observed suggesting the formation of the hydrated salt, [RMIM][anion].XH_2O.

Diels-Alder Reaction between Methyl Acrylate and Cyclopentadiene

The Diels-Alder reaction between methyl acrylate and cyclopentadiene (Figure 3) was performed based on prescribed procedures using a series of polar ionic liquids [RMIM]OAc and in the following solvents: water, methanol, and benzene for comparison. The reactants and the solvent were placed in a screw-capped vial and the reaction was ran for six hours at 60°C with constant stirring. The product obtained was a clear, colorless liquid of a distinct aromatic odor. The product was observed to form a separate phase from the ionic liquid solvent as expected of a relatively non-polar cycloadduct. Thus the separation of product from the mixture only required simple decantation; further extraction with a non polar solvent such as hexane was done to ensure that all of the products were isolated from the reaction mixture.

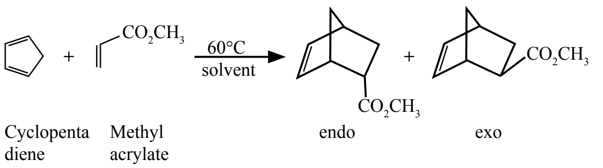

Figure 3 . Diels-Alder reaction between cyclopentadiene and methyl acrylate.

The product yield is observed to decrease as the length of the alkyl R substituent on the imidazolium cation [RMIM] is lengthened from C_6 to C_{12}. This increase in product yield is apparently favored by the polarity and/or the H-bonding ability of the ILs as inferred from the yields obtained with the other solvents used: the product yield is observed to decrease as the polarity and the H-bonding ability of the solvent decreases in the following order: H_2O>methanol>benzene.

The product stereoselectivity ratio (endo:exo) was determined through gas chromatography. In this study, the exo-stereoisomer exhibited a retention time of 6.3 min while the endo-stereoisomer appeared at 7.5 min. These results are consistent with previous studies (Aggarwal et al. 2002; Berson et al. 1962; Abbott et al. 2002) showing earlier retention time for the exo-stereoisomer relative to that of the endo-stereoisomer. The results reflect a high endo-selectivity for the products obtained with [HMIM] OAc as well as a sudden drop in selectivity as the alkyl substituent on the imidazolium cation is lengthened from C_6 to C_8. Furthermore, better endo-selectivity in products is obtained from hydrogen-bond forming solvents (water, methanol) compared with a non-hydrogen bond forming solvent (benzene) as shown by the results in Table 1.

The effect of solvents on the selectivity of the Diels-Alder reaction depends on the individual nature of the diene and the dienophile. The reaction system of interest involves a carbonyl containing dienophile (methyl acrylate) and a cyclic diene (cyclopentadiene) so that only the dienophile is capable of forming hydrogen bonds with the solvent. The hydrogen bond donating ability of the imidazolium cation [RMIM] is

Table 1. Product yield obtained for the Diels-Alder reaction and the stereoselectivity of the DA adduct between cyclopentadiene and methyl acrylate in various solvents.

Solvents		% Yield of Products	Endo:Exo
Ionic Liquid Series,[RMIM] OAc	[HMIM] OAc[a]	89	91:09
	[OMIM] OAc[b]	80	74:26
	[DMIM] OAc[c]	76	76:24
	[DDMIM] OAc[d]	71	79:21
Other solvents	H_2O	91	76:24
	methanol	81	79:21
	benzene	64	74:26

[a] R group: Hexyl (C_6), [b] R group: Octyl (C_8)
[c] R group: Decyl (C_{10}), [d] R group: Dodecyl (C_{12})

reported (Aggarwal et al. 2002) to play a significant role in the stereoselectivity control of the reaction between cyclopentadiene and methyl acrylate. Figure 4a shows that the imidazolium cation, by forming a hydrogen bond with the carbonyl oxygen of methyl acrylate, acts as Lewis acid to favor the endo transition state. The orientation of the component dipoles of the cyclopentadiene and methyl acrylate in the endo- and exo- transition states as shown in Figure 4b suggests that the endo TS has a net dipole moment due to the adding up of the dipoles, while the exo TS has a zero dipole moment due to the cancellation of the dipoles. Therefore, the endo TS is the one favored by the IL, which is a highly polar and ionic solvent.

This hydrogen bond formed between the ionic liquid cation and the methyl acrylate is actually a Lewis acid-Lewis base interaction which is moderated by the hydrogen bond acceptor ability of the ionic liquid anion. That the cation hydrogen can bond with the methyl

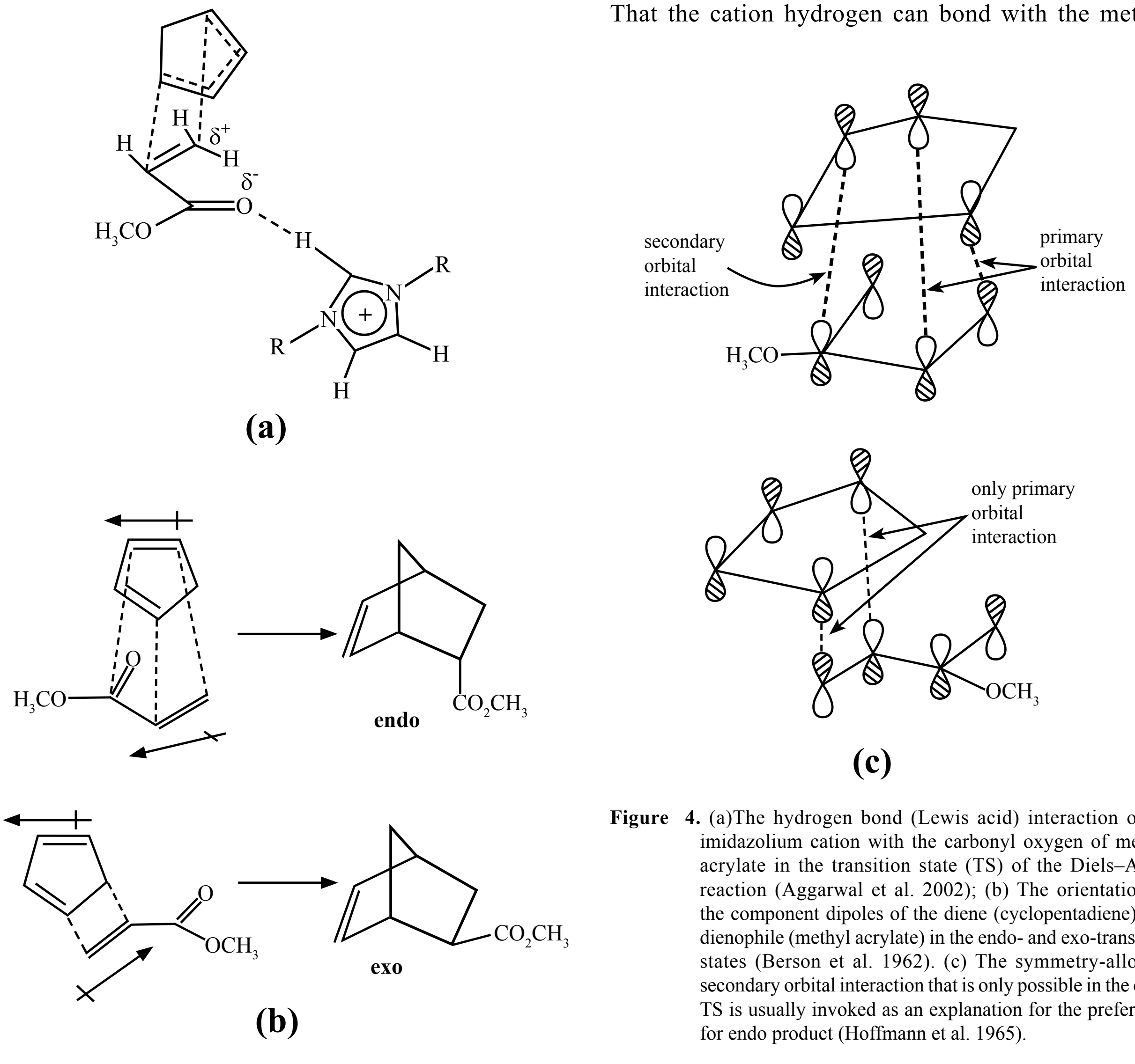

Figure 4. (a)The hydrogen bond (Lewis acid) interaction of an imidazolium cation with the carbonyl oxygen of methyl acrylate in the transition state (TS) of the Diels–Alder reaction (Aggarwal et al. 2002); (b) The orientation of the component dipoles of the diene (cyclopentadiene) and dienophile (methyl acrylate) in the endo- and exo-transition states (Berson et al. 1962). (c) The symmetry-allowed secondary orbital interaction that is only possible in the endo TS is usually invoked as an explanation for the preference for endo product (Hoffmann et al. 1965).

acrylate and the anion as determined by two competing equilibria (Figure 5) has been reported in the literature (Aggarwal et al. 2002).

The lowering of the endo-selectivity of the Diels-alder reactions between methyl acrylate and cyclopentadiene in the following ILs: [OMIM]OAc, [DMIM]OAc and [DDMIM]OAc relative to [HMIM]OAc may be attributed to steric effects. Energy minimization modeling using MM2 (Chem Draw Ultra 9.0) showed that the methyl acrylate is oriented towards RMIM and cyclopentadiene as in Figure 6a and c. Reactions of an alkene with a diene are of a suprafacial-suprafacial nature. The orientation of the [HMIM] cation, relative to the methyl acrylate and cyclopentadiene is shown in Figure 6b. The imidazole C_2-H is interacting with the C=O of the methyl acrylate where the C=C tail of the acrylate is syn to the R group (C_6). This kind of arrangement among the three molecules allows for a symmetry-allowed secondary orbital interaction (Hoffmann & Woodward 1965) between C_2 of cyclopentadiene and C=O of methyl acrylate which is characteristic of a transition state that gives rise to an endo product. As the R group is lengthened, the MM2 modeling showed that the R chain started bending towards the cyclopentadiene-methyl acrylate pair. For more effective interaction, this diene-methyl acrylate pair twisted to make the longer R group syn with the CH_3OCO- group such that a secondary orbital interaction between C_2 of

$$[\text{RMIM}]^{+} + \text{OAc} \overset{k_1}{\rightleftharpoons} [\text{RMIM}]^{+} \text{ ---- } {}^{-}\text{OAc} \qquad (1)$$

$$[\text{RMIM}]^{+} + \text{MA} \overset{k_2}{\rightleftharpoons} [\text{RMIM}]^{+} \text{ ---- } \text{MA} \qquad (1)$$

Figure 5. The two competing equilibria in the Diels-Alder reaction of methyl acrylate (MA) and cyclopentadiene in [RMIM] OAc medium.

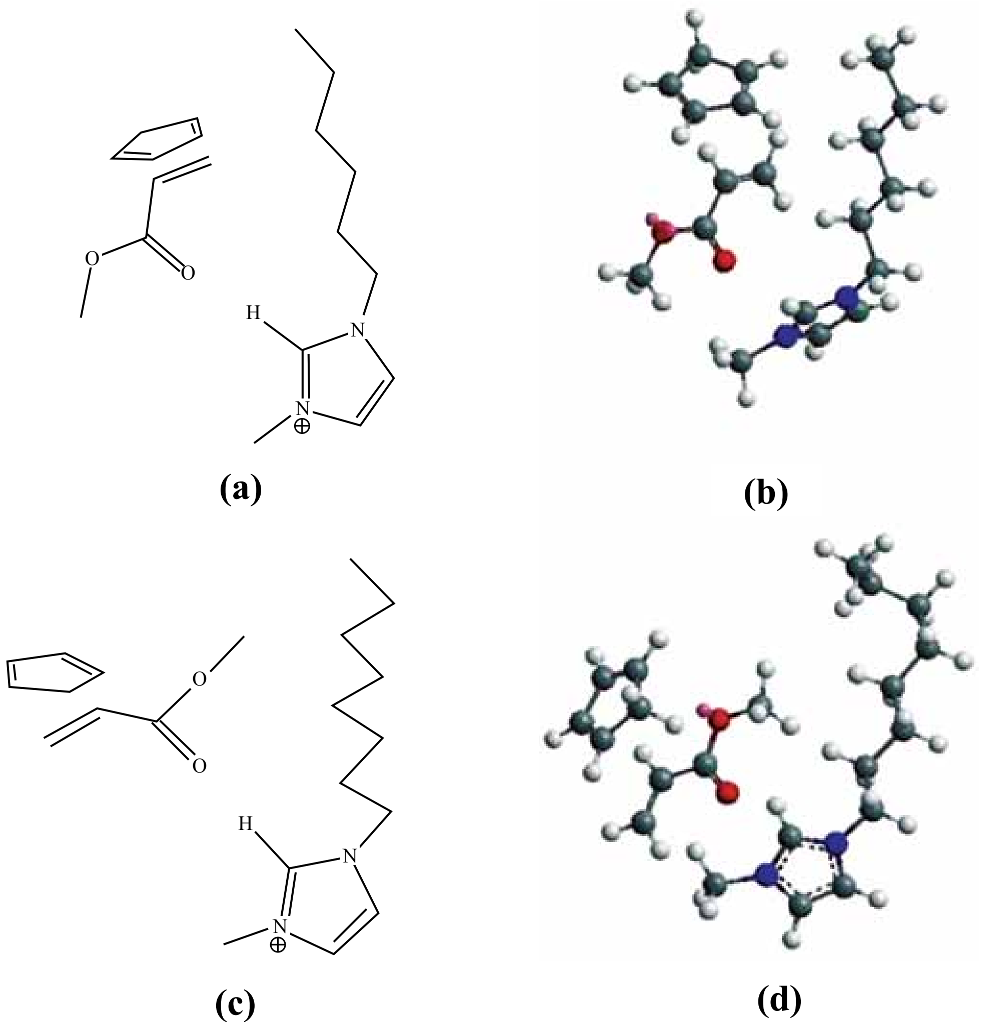

Figure 6. Representations of the endo- and exo- TS in the Diels-Alder reaction of methyl acrylate and cyclopentadiene in [RMIM]OAc medium; (a) and (c) are 2D models of endo TS and exo TS, respectively; (b) and (d) are 3D models of endo TS and exo TS, respectively.

cyclopentadiene and C=O of methyl acrylate became less effective. Therefore, the product obtained was the exo isomer, instead of the endo product.

CONCLUSION

A polar halogen-free IL series, [RMIM]OAc has been successfully synthesized. The efficiency of the Diels-Alder reaction between methyl acrylate and cyclopentadiene in [RMIM]OAc solvent has been evaluated and cross-comparison in the series shows the use of [HMIM]OAc to be most efficient in terms of product yield and endo-stereoselectivity. It is noteworthy that the product yield obtained with [HMIM]OAc (89%) does not exceed that obtained with water (91%), a green alternative solvent for the reaction of interest, but the difference is quite minimal. The product endo-stereoselectivity obtained with [HMIM] OAc (91:9) remarkably exceeds that obtained with water (76:24); [HMIM]OAc apparently greatly enhanced the formation of the endo product. In addition, the separation of the product from this IL reaction medium only requires simple work-up procedure. The halogen-free ionic liquid [HMIM]OAc has thus been demonstrated as an effective green alternative media for the Diels-Alder reaction between cyclopentadiene and methyl acrylate.

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REFERENCES

ABBOTT AP, CAPPER G, DAVIES DL, RASHEED RK, TAMBYRAJAH V. 2002. Quaternary Ammonium Zinc- or Tin- Containing Ionic Liquids: Water Insensitive, Recyclable Catalysts for Diels Alder Reactions. Green Chemistry, 4, 24-26.

AGGARWAL A, LANCASTER NL, SETHI AR, WELTON T. 2002, The role of hydrogen bonding in controlling the selectivity of Diels–Alder reactions in room-temperature ionic liquids. Green Chemistry 4, 517–520.

BERSON JA, HAMLET Z, MUELLER, WA. 1962. The Correlation of Solvent Effects on the Diels Alder Reactions by Means of Linear Free Energy Relationships. A New Empirical Measure of Solvent Polarity. J Am Chem Soc 84, 297-304.

CLARKE D, ALI M, CLIFFORD A, PARRATT A, ROSE P, SCHWINN D, BANNWARTH W, RAYNER C. 2004. Reactions in Unusual Media. Current Topics in Medicinal Chemistry 4, 729-771.

EARL MJ, MCCORMAC PB, SEDDON KR 1998. Diels-Alder Reaction in Ionic Liquids. Chem Commun 71 2245-2246.

FISHER T, SETHI T, WELSON T, WOOLF J. 1999. Diels-Alder Reaction in Room Temperature Ionic Liquids. Tetrahedron Lett 40, 793-796.

GARRETT RH, GRISHAM CM. 2005. Biochemistry. Singapore: Brooks/Cole, Thomson Learning Asia. 1085p.

HOFFMANN R, WOODWARD RB. 1965. Orbital Symmetries and Endo-Exo Relationships in Concerted Cycloaddition Reactions. J Am Chem Soc 87, 4388-89.

HOLBREY JD, SEDDON KR. 1999. Ionic Liquids. Clean Products and Processes 1: 223-236.

JAEGER DA, TUCKER CE. 1989. Diels-Alder Reactions in Ethylammonium Nitrate, A Low-Melting Fused Salt. Tetrahedron Lett 30: 1785-1788.

KOEL M. 2000. Physical and Chemical Properties of Ionic Liquids Based on the Dialkylimidazolium Cations. Proc Estonian Acad Sci Chem 49(3), 145-155.

OLIVIER-BOURBIGOU H, MAGNA L. 2002. Ionic Liquid Perspectives for Organic and Catalytic Reactions. J Molecular Catalysis A: Chemical 3484. 1–19.

SEDDON KR.1998. Ionic Liquids for Clear Technology. In: Molten Salt Forum. Proceedings of 5th International Conference on Molten Salt Chemistry and Technology, Vol. 5-6. Wendt H. (ed); 1988 August; Dresden, Germany: Trans Tech Publications, Inc. p. 53-62.

WELTON T. 1999. Room Temperature Ionic Liquids: Solvents for Synthesis and Catalysis. Chemical Reviews 99, 2071-2083.