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Moisture Stable Dialkylimidazolium Salts as Heterogeneous and Homogeneous Lewis Acids in the Diels-Alder Reaction

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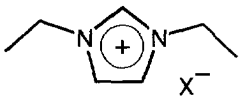
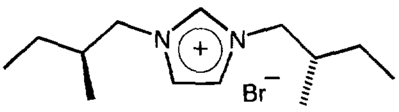
Abstract: Moisture stable dialkylimidazolium salts act as heterogeneous and homogeneous Lewis acid catalysts in the Diels-Alder reaction of both crotonaldehyde and methacrolein with cyclopentadiene at low temperatures. The heterogeneous system allows the catalyst to be efficiently recycled. © 1997 Elsevier Science Ltd.

In our search for new classes of homochiral Lewis acids we have carried out a preliminary investigation into the Lewis acid activity of moisture stable dialkylimidazolium salts ($R_2Im^+ X^-$). These salts often behave as ionic liquids or are solids with very low melting points and are an unconventional and interesting class of compounds. Although there has been a great deal of interest in ionic liquids, a survey of the literature shows that to date the overwhelming majority of publications concerning these compounds deal with the physical properties of these systems, such as conductivity[1] and stability.[2] There are a few recent publications concerning their use in polymerisation and hydrogenation catalysis,[3,4] however the ionic liquids used in these reactions are generally moisture sensitive and as such will have a limited use. We are interested in the water stable salts such as the dialkylimidazolium bromides and trifluoroacetates as Lewis acid catalysts, as these might have a wide appeal in synthesis. We are also interested in using the dialkylimidazolium cation as the Lewis acid centre rather than using these ionic liquids as solvents for Lewis acids or other reactive species which has always been the case to date.



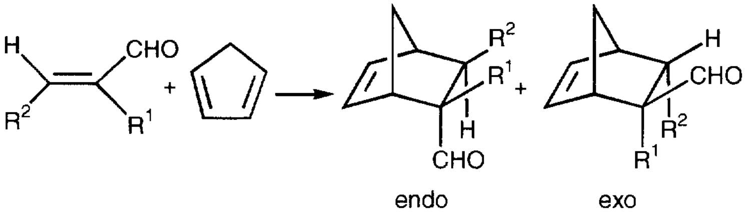
1 X = Br, **2** X = CF_3COO



3

In this communication we demonstrate that dialkylimidazolium salts may be used as Lewis acids and that one of these Lewis acids is reusable under heterogeneous catalysis conditions.

We investigated the Lewis acidity of three dialkylimidazolium salts, compounds **1** to **3**, in the Diels-Alder reaction between crotonaldehyde **4** or methacrolein **5** with cyclopentadiene **6**, Scheme 1. The diethylimidazolium bromide **1** was produced in a yield of 46% and the diethylimidazolium trifluoroacetate **2** was produced in 89% yield from **1** on addition of silver trifluoroacetate to an aqueous solution of **1** following the method of Harlow *et al.*[5] The use of these particular Diels-Alder reactions allows comparisons to be made with other work in the Lewis acid area.



4 $R^1 = H, R^2 = Me$ **6** **7** $R^1 = H, R^2 = Me$

5 $R^1 = Me, R^2 = H$ **8** $R^1 = Me, R^2 = H$

Scheme 1

The dialkylimidazolium salts, **1**, **2** or **3**[6] (0.2 equivalents) were stirred in dichloromethane for 48h with the dienophile **4** or **5** (1.0 equivalent) and the diene (5.0 equivalents), at -25 °C, under nitrogen. All six reactions produced the desired products **7** or **8** (endo and exo) in yields between 35 and 40%. The endo:exo selectivities for the crotonaldehyde/cyclopentadiene reactions were always greater than 90:10 and those for the methacrolein/cyclopentadiene reactions were always greater than 15:85 (endo:exo ratios were determined by proton NMR from the integration ratios of the aldehydic protons), Table 1. The control reactions between methacrolein or crotonaldehyde and cyclopentadiene without the dialkylimidazolium salt present gave no product after 48h at -25 °C.

These results show clearly that these dialkylimidazolium salts act as Lewis acids, both in the way that they catalyse the two Diels-Alder reactions at low temperature and the high endo : exo selectivities relative to the non catalysed reactions. However, the yields show that they are weak Lewis acids, but there is obvious scope to increase the Lewis acidity by using electron withdrawing groups, such as chloro, bromo, cyano and nitro, on the carbons of the imidazole ring or an aryl/alkyl sulfonyl group on one of the nitrogens in the ring.

Table 1. Results (Yield%; Endo:Exo Ratio) for the Diels-Alder Reaction Between Cyclopentadiene and Crotonaldehyde or Methacrolein in the Presence of Dialkylimidazolium Salts **1**, **2** or **3**.

	Dienophile	
Dialkylimidazolium Salt	**Crotonaldehyde**	**Methacrolein**
1	35%; 95 : 5	40%; 15 : 85
2	37%; 95 : 5	40%; 13 : 87
3	36%; 93 : 7	36%; 10 : 90

An interesting property of the dialkylimidazolium salt **1** is the ease with which it can be recycled under heterogeneous conditions. The above reactions were carried out in dichloromethane, in which **1** is soluble. However ionic liquid **1** does not dissolve in diethyl ether and remains fluid at -25 °C. A heterogenous reaction between crotonaldehyde and cyclopentadiene in the presence of **1**, under the same conditions as before, except substituting diethyl ether for dichloromethane as the reaction solvent, gave a 25% yield of the product **7** (endo and exo). The diethyl ether layer was decanted off and the remaining **1** was washed with further diethyl ether. This process was repeated four more times and gave approximately the same yield of products (24, 23, 23 and 21% respectively).

Our attempts at carrying out catalytic asymmetric Diels-Alder reactions using the homochiral *N*,*N*-di(2'*S*-2'-methylbutane)imidazolium bromide[6] catalyst **3**, synthesised in a similar manner to **1**, in 21% yield by heating the readily available *S*-(+)-1-bromo-2-methylbutane with TMS-imidazole at reflux temperature, were not successful as the enantiomeric excesses achieved in the reactions (Scheme 1) were less than 5% (as determined by chiral GC).

We are continuing investigations in this area with dialkylimidazolium salts containing electron withdrawing groups in the imidazole ring, with other homochiral dialkylimidazolium salts and with other Lewis acid mediated reactions such as Claisen rearrangements,[7] the ene reaction[8] and cyanohydrin formation[9] with the intent to produce a new and efficient class of homochiral Lewis acid catalysts.

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References and Notes:

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6. Prepared *via* the method in reference 5, and is consistent with the ^{1}H- and ^{13}C-NMR data; ^{1}H-NMR (400MHz, Acetone d_6) 0.93 (6H, t, J= 7.4Hz, 4'-CH_3), 1.25 (2H, m, 3'-CH_2), 1.4 (2H, m, 3'-CH_2), 2.1 (6H, d, J= 6.9Hz, 2'-CH$\mathit{CH_3}$ overlapping 2H, m, 2'-CH), 4.38 (4H, m, NCH_2), 7.88 (2H, s, 4-and 5-CH (Im)), 10.03 (1H, s, 2-H (Im)) ppm; ^{13}C-NMR (100MHz, $CDCl_3$) 10.47, 15.88, 20.89, 25.83, 35.15, 122.26, 136.56 ppm. $[\alpha]^{25}_D = +19^\circ$ (c = 6, $CHCl_3$).
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