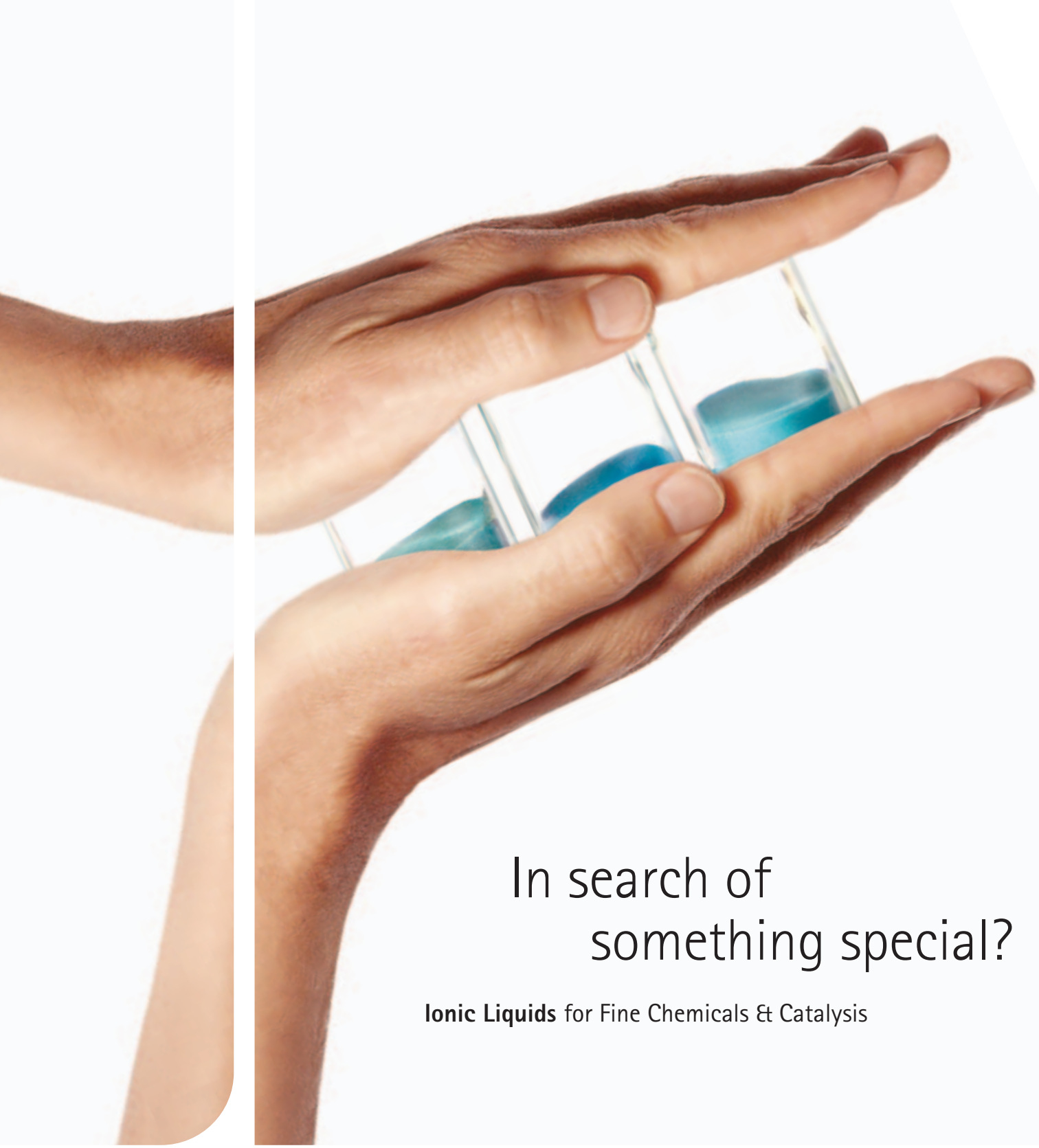

In search of something special?

Ionic Liquids for Fine Chemicals & Catalysis

MERCK

Catalyze your chemical syntheses and make your processes "greener" ...

Ionic Liquids, innovative salts with melting points below 100 °C, offer the option of tunable properties generating the potential to get improved solvent systems for chemical reactions. These materials consist entirely of ions often being liquid at room temperatures.

Advanced properties beneficial for fine chemistry, like comparably high polarities and negligible vapor pressure, make Ionic Liquids the perfect materials for these processes. Your benefits resulting from these unique properties can be achieved by using Ionic Liquids as an immobilizer of a transition metal catalyst, as solvent or co-solvent or even as a catalyst itself.

Merck Ionic Liquids: The right choice for you.

- Together with us you are well positioned to deal with the challenges of creating the basis today for your success tomorrow.
- By reliably supplying you with materials on a continuous high quality level according to specification.
- From the initial idea to a multi ton production scale, all from one hand giving you the opportunity to support you in all regulatory affairs like GHS and REACH.

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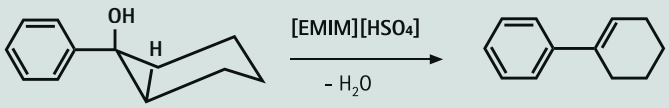
Brønsted acid catalysis

Brønsted acidic Ionic Liquids as catalytic system

Dehydration of alcohols in Ionic Liquids

Synthesis of 1-Phenylcyclohex-1-en



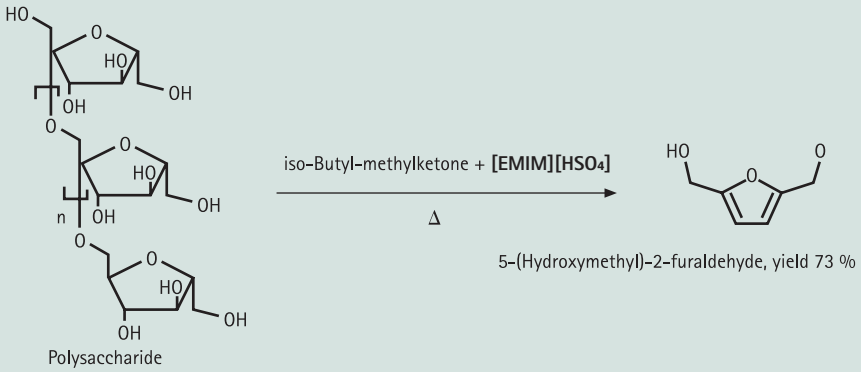
Ref.: N. Ignatyev, M. Schulte, K. Koppe, P. Barthen, S. Zlotin, N. Makhova, A. Sheremetev, A. Valente, Phosphorus, Sulfur, and Silicon and the Related Elements, (2011) accepted

Advantages:

- Product can be easy separated by decantation or destillation
- Ionic Liquid can be reused several times (up to 10 times)
- High overall yield (> 90 %) in a short reaction time
- Effective without additional Brønsted acid

Conversion of mono/di/polysaccharides into furan compounds

Synthesis of HMF from Inulin



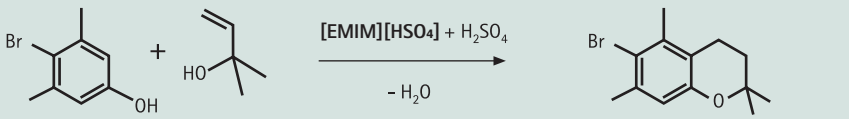
Ref.: S. Lima, P. Neves, M. M. Antunes, M. Pillinger, N. Ignatyev, A. A. Valente, Applied Catalysis (2009) 93-99

Using Brønsted acidic Ionic Liquids prevents the use of environmentally questionable chromium salts thereby achieving high yields compared to conventional HMF synthesis routes.

Synthesis of chromane derivatives in Ionic Liquids

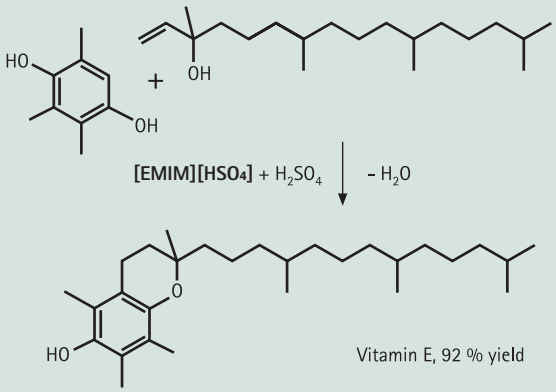
Volatile Brønsted acids, dissolved in Ionic Liquids with the same counter anion, stay in the system even at temperatures well above the boiling point of the Brønsted acid.

Synthesis of 6-Bromo-2,2,5,7-tetramethylchromane



6-Brome-2,2,5,7-tetramethylchromane, 89 % yield

Synthesis of (Vitamin E) (DL- α-Tocopherole)

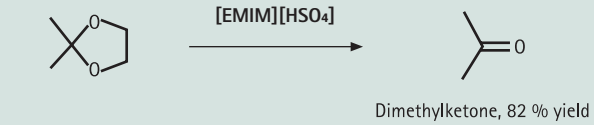


Vitamin E, 92 % yield

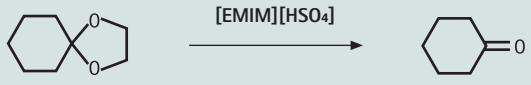
Synthesis was optimized by the application of biphasic system: Ionic Liquid/hexane. Ionic Liquid can be re-used several times.

Ketals splitting in Ionic Liquids

Synthesis of Dimethylketone and Cyclohexanone



Dimethylketone, 82 % yield



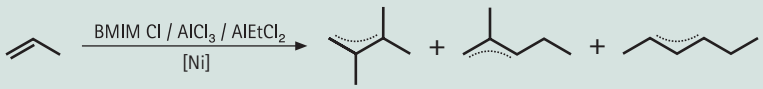
Cyclohexanone, 63 % yield

Lewis acid catalysis

Activation of catalysts by increasing the electrophilicity

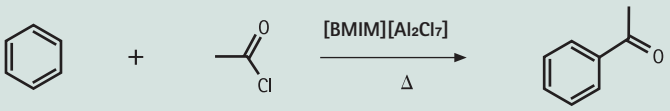
Combining certain Ionic Liquids (ILs) with specific catalysts under slightly acidic conditions can initiate the activation of catalysts by increasing the electrophilicity of the catalytic center. Examples of such effects can be found in the following published reaction schemes. The increase of reaction selectivity, a reduction of reaction time or increase in product yield can be analyzed from the cited publications.

Propene dimerization in chloroaluminate IL



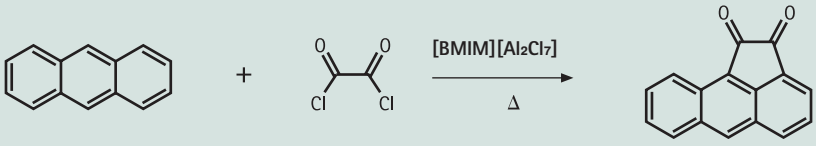
Ref. F. Favre, A. Forestire, F. Hugues, H. Olivier-Bourbigou, J.A. Chodorge, Oil Gas Eur. Mag. 2 (2005) 83

Friedel-Crafts Acylation of benzene with acetylchloride to form acetophenone



Ref.: Changzhi Li, Wujun Liu, Zongbao (Kent) Zhao, Catalysis Communications 8 (2007) 1834-1837

Friedel-Crafts Acylation of anthracene with oxalyl chloride to form 1,2-aceanthrylenedione



Ref.: Yuan Xin-huaa, Chen Minb, Cheng Xiao-nonga, Chemical Engineering Journal 146 (2009) 266-269

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markus.wagner@merckgroup.com

Ordering information

Productname	Short name	Cat. No.	Quality
1-Ethyl-3-methylimidazolium hydrogensulfate	[EMIM][HSO_4]	490223	S
1-Butyl-3-methylimidazolium heptachloroaluminate	[BMIM][Al_2Cl_7]	490326	S

Further reading/References:

Brønsted acid catalysis

Ionic liquids and catalysis: recent progress from knowledge to applications
H. Olivier-Bourbigou, L. Magna, D. Morvan,
Applied Catalysis A: General 373(2010)1-56

Conversion of mono/di/polysaccharides into furan compounds using
1-alkyl-3-methylimidazolium ionic liquids.
S. Lima et.al., Applied Catalysis A, **(2009)** *93-99*

Solvent-free synthesis of benzoic esters and benzyl esters in novel
Brønsted acidic ionic liquids under microwave irradiation.
X Li, e.a., Catalysis Communications 9 **(2008)** *2264-2268*

Acidic ionic liquid [BMIM][HSO_4]: An efficient catalyst for acetalization and
thioacetalization of carbonyl compounds and their subsequent deprotection.
N. Gupta e.a., Catalysis Communications 8 **(2007)** *1323-1328*

Brønsted acidic ionic liquids: A green, efficient and reusable catalyst system and
reaction medium for Fischer esterification.
T. Joseph e.a., Journal of Molecular Catalysis A: Chemical 234 **(2005)** *107-110*

Lewis acid catalysis

Nickel-catalyzed dimerisation of propene in chloroaluminate ionic liquids.
M. Eichmann, W. Keim, M. Haumann, B. Melcher, P. Wasserscheid Journal of Molecular Catalysis A: Chemical, 314 (2009), 42-48

Friedel-Crafts acylation af anthracene with oxalyl chloride catalyzed by ionic liquid of [BMIM]Cl/$AlCl_3$
Y. Xin-hua e.a., Chemical Engineering Journal 146 **(2009)** *266-269*

Detailed kinetic study of cumene isopropylation in a liquid-liquid biphasic system using acidic chloroaluminate ionic liquids.
J. Joni e.a., Journal of Catalysis 258 **(2008)** *401-409*

Evaluation Lewis acid catalyzed hydroalkylation of alkenes in neat and in ionic liquids.
H. E. Lanman e.a., Journal of Molecular Catalysis A: Chemical 279 **(2008)** *218-222*

Isobutane/2-butene alkylation catalyzed by chloroaluminate ionic liquids in the presence of aromatic additives.
J. Zhang e.a., Journal of Catalysis 249 **(2007)** *261-268*

Efficient synthesis of benzophenone derivatives in Lewis acid ionic liquids.
C. Li e.a., Catalysis Communications 8 **(2007)** *1834-1837*

Coumarin syntheses via Pechmann condensation in Lewis acidic chloroaluminiate ionic liquid.
M. K. Potdar e.a., Tetrahedron Letters 42 **(2001)** *9285-9287*

Catalyzing Henry reaction in chloroaluminate ionic liquids.
A. Kumar e.a., Journal of Melecular Catalysis A: Chemical 235 **(2005)** *244-248*

Arene carbonylation in acidic, chloroaluminate ionic liquids.
E. J. Angueira e.a., Journal of Molecular Catalysis A: Chemical 227 **(2005)** *51-58*

Friedel-Crafts acylation of aromatics catalysed by supported ionic liquids.
M. H. Valkenberg e.a., Applied Catalysis A: General 215 **(2001)** *185-190*

Example fields of application

Brønsted acid catalysis

- Dehydration of alcohols
- Synthesis of Vitamin E
- Ketal splitting
- Synthesis of HMF from polysaccharides

Lewis acid catalysis

- Olefin Dimerization
- Friedel-Crafts Acylation
- Synthesis of acetophenon from benzene
- Synthesis of 1,2-aceanthrylenedione from anthracene

Ionic Liquids in acid catalysis

The following examples should be read as information to the broad utility of ILs for acid catalysis or in combination with catalysts (composite ionic liquids). Possible rights of third parties related to such examples may exist.

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