



## A Review on

*First title: Ionic liquids-useful reaction green solvents for the future*

*Second title: ionic liquids are the replacements for environmentally damaging solvents in a wide range of chemical processes.*

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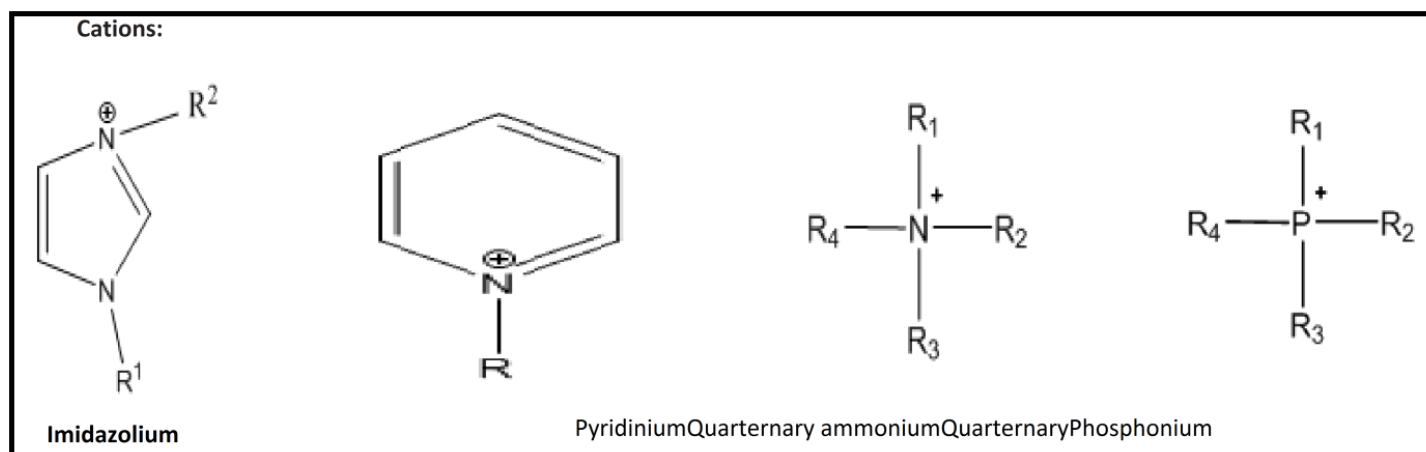
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**Summary:**

Ionic liquids (IL) represent a fascinating new class of solvents with unusual physical and chemical properties; low melting salts (up to 100°C). The main driving force for research in this area is the need to find replacement for environmentally damaging solvents in a wide range of chemical processes. To date, most chemical reactions have been carried out in molecular solvents. For the past twenty years, most of our understanding of our chemistry has been based upon the behavior of molecules in the solution phase in molecular solvents. Recently a new class of solvents has emerged called as Ionic liquids. An ionic liquid is an organic salt in which the ions are poorly coordinated, which results in these solvents being liquid below 100°C, or even at room temperature (room temperature ionic liquids, RTIL's). At least one ion has a delocalized charge and one component is organic, which prevents the formation of a stable crystal lattice. Ionic liquids are composed entirely of ions. For example, molten sodium chloride is an ionic liquid; in contrast, a solution of sodium chloride in water (a molecular solvent) is an ionic solution. The term "ionic liquids" has replaced the older phrase "molten salts" (or "melts"), which suggests that they are high-temperature, corrosive, viscous media (like molten minerals). The reality is that ionic liquids can be liquid at temperatures as low as -96°C. Furthermore, room-temperature ionic liquids are frequently colourless, fluid, and easy to handle. In the patent and academic literature, the term "ionic liquids" now refers to liquids composed entirely of ions that are fluid around or below 100°C<sup>1</sup>. Properties, such as melting point, viscosity, and solubility of starting materials and other solvents, are determined by the substituents on the organic component and by the counter ion. Many ionic liquids have even been developed for specific synthetic problems. For this reason, ionic liquids have been termed "designer solvents". This means that their properties can be adjusted to suit the requirements of a particular process. Properties such as melting point, viscosity, density, and hydrophobicity can be varied by simple changes to the structure of the ions. For example, the melting points of 1-alkyl-3-methylimidazolium tetrafluoroborates and hexafluorophosphates are a function of the length of the 1-alkyl group, and form liquid crystalline phases for alkyl chain lengths over 12 carbon atoms. Another important property that changes with structure is the miscibility of water in these ionic liquids. For example, 1-alkyl-3-methylimidazolium tetrafluoroborate salts are miscible with water at 25 °C where the alkyl chain length is less than 6, but at or above 6 carbon atoms, they form a separate phase when mixed with water. This behaviour can be of substantial benefit when carrying out solvent extractions or product separations, as the relative solubility's of the ionic and extraction phase can be adjusted to make the separation as easy as possible. In addition, ionic liquids have practically no vapour pressure which facilitates product separation by distillation. There are also indications that switching from a normal organic solvent to an ionic liquid can lead to novel and unusual chemical reactivity. This opens up a wide field for future investigations into this new class of solvents in catalytic applications. Research into ionic liquids is booming. The first industrial process involving ionic liquids was announced in March 2003, and the potential of ionic liquids for new chemical technologies is beginning to be recognized. One of the primary driving forces behind research into ionic liquids is the perceived benefit of substituting traditional industrial solvents, most of which are volatile organic compounds (VOCs), with non-volatile ionic liquids. Replacement of conventional solvents by ionic liquids would prevent the emission of VOCs, a major source of environmental pollution. Ionic liquids are not intrinsically "green"—some are extremely toxic—but they can be designed to be environmentally benign, with large potential benefits for sustainable chemistry. There are four principal strategies to avoid using conventional organic solvents: No solvent (heterogeneous catalysis), water, supercritical fluids, and ionic liquids. The solventless option is the best established, and is central to the petrochemical industry, the least polluting chemical sector. The use of water can also be advantageous, but many organic compounds are difficult to dissolve in water, and disposing of contaminated aqueous streams is expensive<sup>2</sup>. Supercritical fluids, which have both gas- and liquid-like properties, are highly versatile solvents for chemical synthesis.

This technology was recently commercialized by Thomas Swan & Co., Ltd., in a chemical plant designed for multipurpose synthesis. Together with ionic liquids, these alternative solvent strategies (sometimes referred to as alternative reaction media or green solvents) provide a range of options to industrialists looking to minimize the environmental impact of their chemical processes. What are the advantages of using a room-temperature ionic liquid in an industrially relevant catalytic process? As noted above, ionic liquids have no detectable vapour pressure, and therefore contribute no VOCs to the atmosphere. But this is not the only reason for using ionic liquids. Another is that at least a million binary ionic liquids, and  $10^{18}$  ternary ionic liquids, are potentially possible<sup>3</sup>. (For comparison, about 600 molecular solvents are in use today.) The next decade should see ionic liquids being used in many applications where conventional organic solvents are used today. Furthermore, ionic liquids will enable new applications that are not possible with conventional solvents. In the future, solvents will be designed to control chemistry, rather than the chemistry being dictated by the more limited range of molecular solvents currently used<sup>4</sup>. As discussed above, ionic liquids are salts consisting of cations such as imidazolium, pyridinium, quarternary ammonium and quarternary phosphonium, and anions such as halogen, triflate, trifluoroborate and hexafluorophosphate, which exists in the liquid state at relatively low temperatures. Their characteristic features include almost no vapour pressure, non-inflammability, non-combustibility, high thermal stability, relatively low viscosity, wide temperature ranges for being liquids and ionic liquid conductivity.

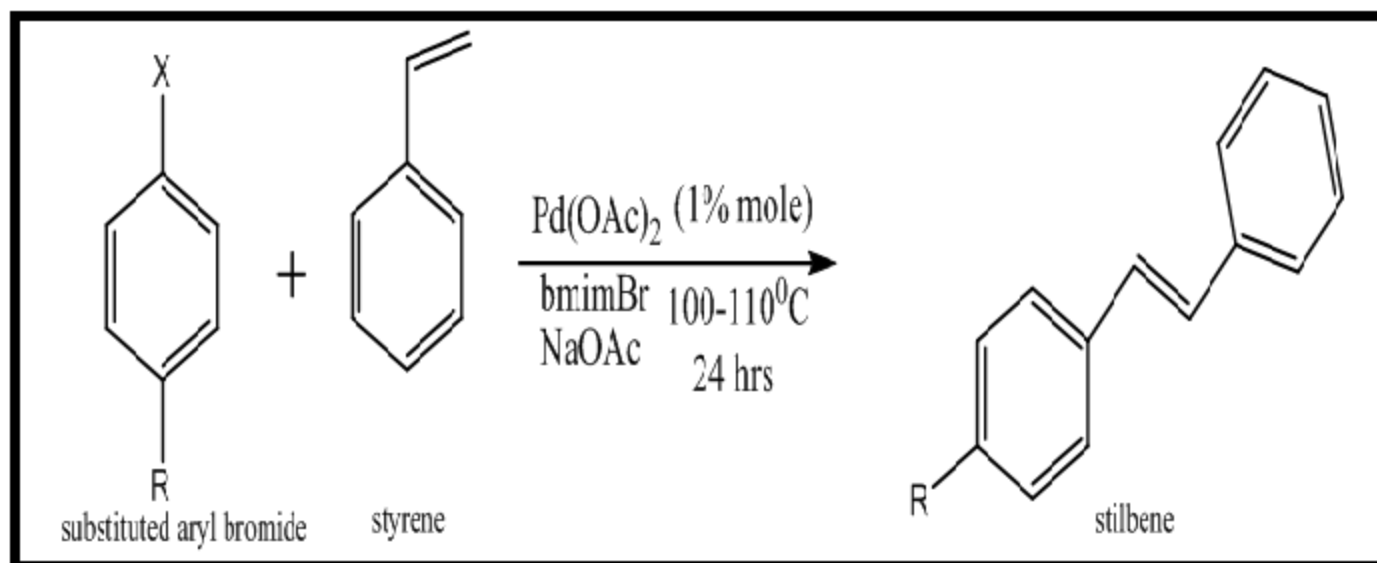
**KEY WORDS:** ionic liquids, green solvents, designer solvents, low melting salts.



**IONIC LIQUIDS ARE USED IN SOME REACTIONS LIKE HECK REACTIONS, SUZUKI-MIYaura COUPLING REACTION, WITTING REACTION, FRIEDEL-CRAFTS REACTION, ALDOL CONDENSATION.**

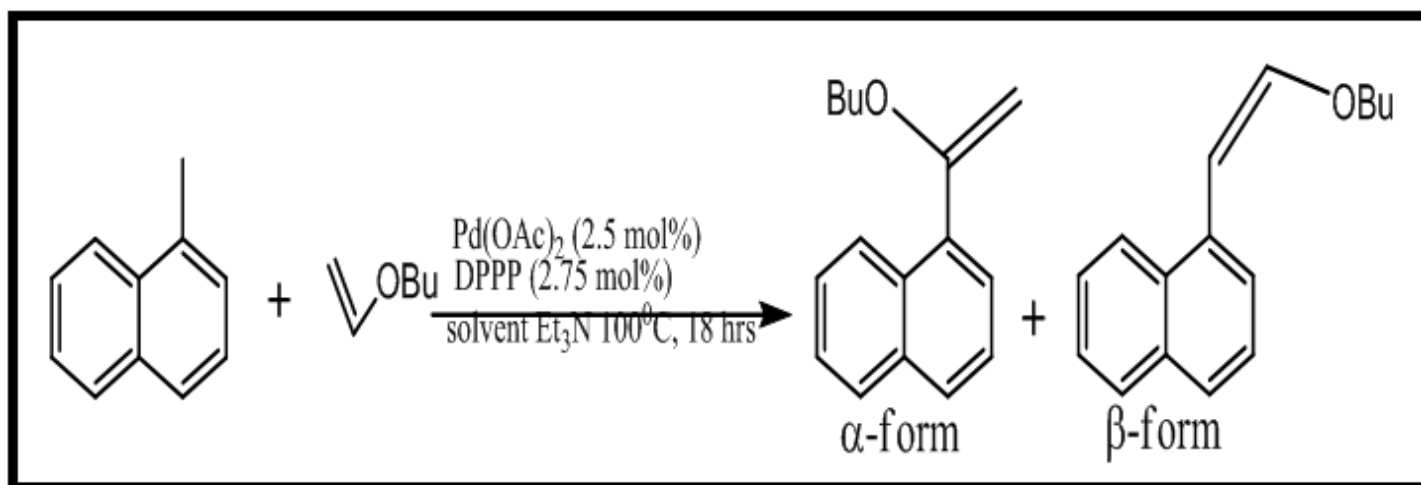
#### HECK REACTION:

In Heck reaction using palladium catalysts, polar solvents such as DMF and acetonitrile are employed and aryl iodides are normally used as substrates. When less reactive aryl bromides or chlorides are employed, more active catalysts like phosphine ligands are added to retain the catalytic activity. By using, 1-butyl-3-methylimidazolium bromide (bmimBr) as solvent, aryl bromides react with styrene to produce stilbenes in high yields without adding a phosphine ligand<sup>5</sup>.



| Entry | X  | R    | Percent Yield |
|-------|----|------|---------------|
| 1     | I  | H    | 99            |
| 2     | Br | CHO  | 90            |
| 3     | Br | MeCO | 88            |

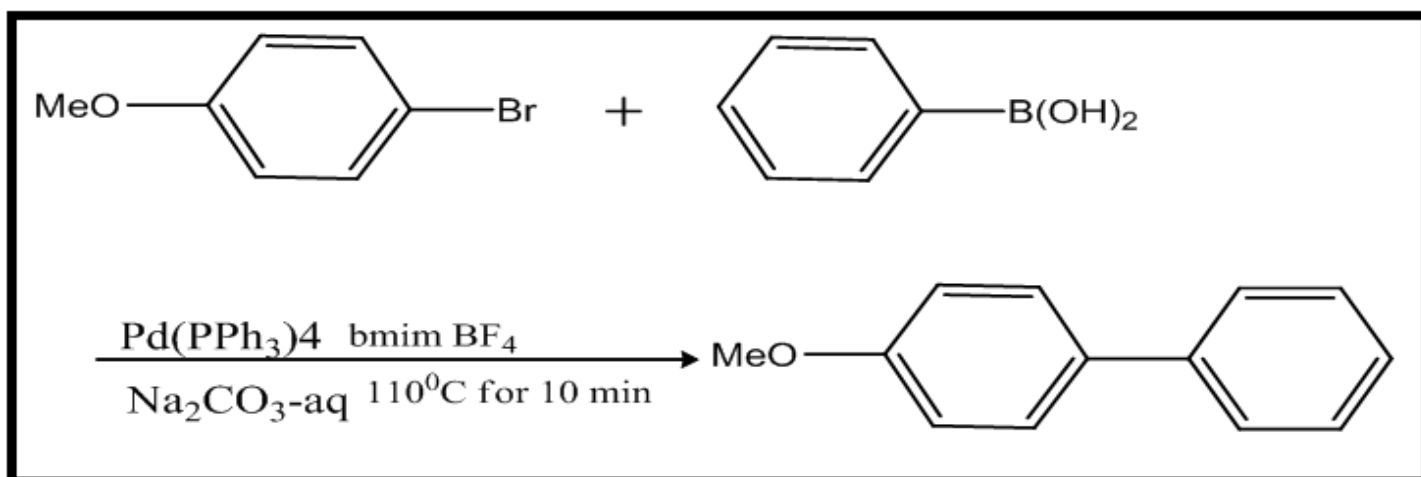
The reactions of enol ethers bearing an electron donating group with aryl halides using bmim BF<sub>4</sub> as solvent gives only  $\alpha$  substituent specifically<sup>6</sup>. In addition heck reaction substituents and  $\beta$ (beta) substituents under normal Heck reaction conditions. However, the reaction of vinyl ethers employing tetrabutylammoniumbromide(Bu<sub>4</sub>NBr), which is quaternary ammonium salt, has been reported<sup>7</sup>.



| Entry | solvent              | Conv(%) | $\alpha/\beta$ |
|-------|----------------------|---------|----------------|
| 1     | Toluene              | 23      | 46/54          |
| 2     | Bmim BF <sub>4</sub> | 50      | >91/1          |
| 3     | Bmim BF <sub>4</sub> | 100     | >99/1          |

#### SUZUKI-MIYAUURA COUPLING REACTION:

In Suzuki-Miyaura coupling reaction where biaryls are produced from aryl halides and aryl boronic acids in the presence of Palladium catalyst and a base. The removal of the catalyst is often a problem. In the system where an ionic liquid is used as solvent, the product can be extracted with ether after the reaction is complete, with catalyst being retained in the ionic liquid. The ionic liquid and the catalyst can then be reused as they are<sup>8</sup>.

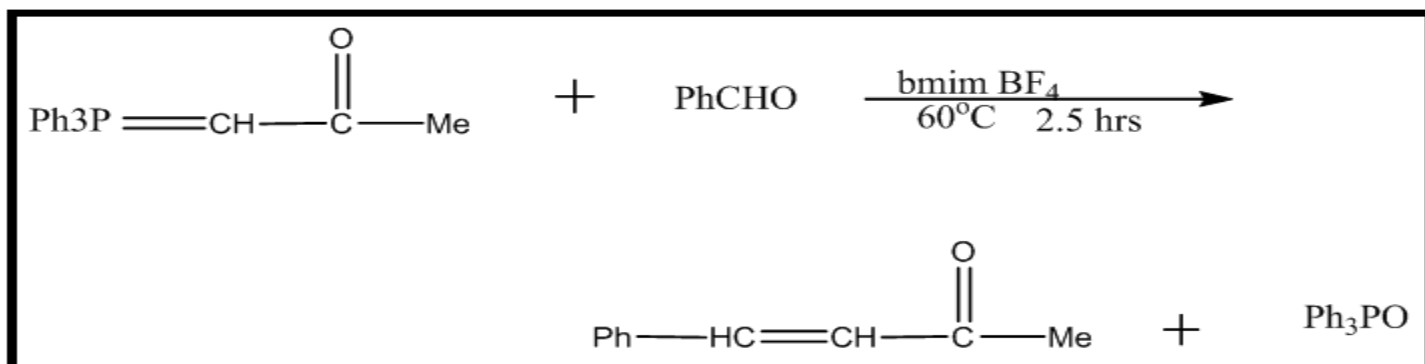


| Entry | Catalytic solution  | Percent Yield |
|-------|---------------------|---------------|
| 1     | 1 <sup>st</sup> use | 81            |
| 2     | 2 <sup>nd</sup> use | 89            |
| 3     | 3 <sup>rd</sup> use | 77            |
| 4     | 4 <sup>th</sup> use | 82            |

**WITTING REACTION:**

It is a useful method for C-C double bond formation. However separation of the product and by-product, triphenylphosphine oxide is a classic problem. The separation and purification are usually carried out by

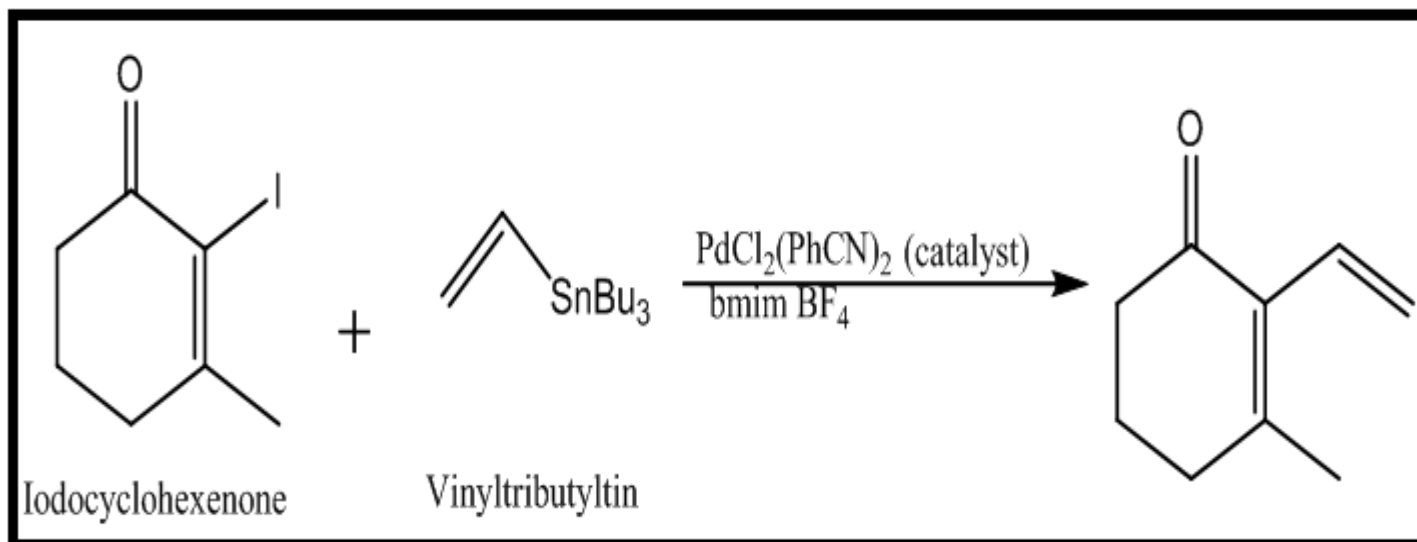
crystallization or chromatography. When an ionic liquid is used as solvent, the product and phosphine oxide can be easily separated by combining an ether extraction and toluene extraction after the reaction is complete. In addition, it is possible to efficiently reuse the ionic liquid<sup>9</sup>.



| Entry | Catalytic solution  | Percent Yield |
|-------|---------------------|---------------|
| 1     | 1 <sup>st</sup> use | 82            |
| 2     | 2 <sup>nd</sup> use | 83            |
| 3     | 6th use             | 91            |

**STILLE REACTION:**

Stille reaction is a useful reaction where an organotin compound and an electrophilic reagent are reacted to form a C-C bond under mild conditions in the presence of palladium catalyst. In the reaction of vinyltributyltin and iodocyclohexenone in an ionic liquid, the product can be



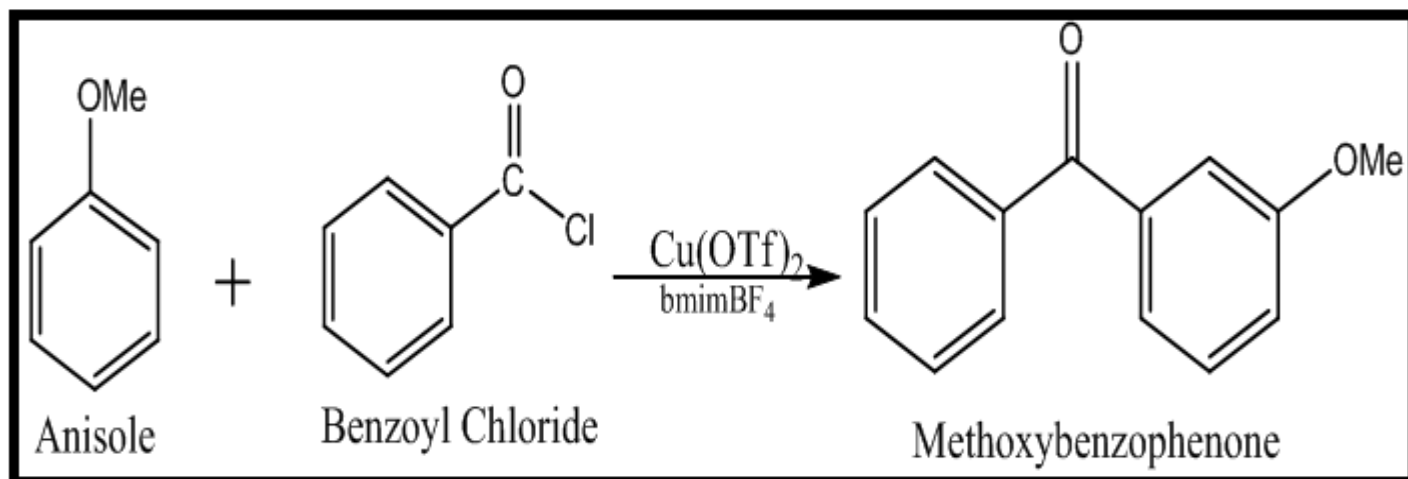
| Entry | Catalytic solution  | Percent Yield |
|-------|---------------------|---------------|
| 1     | 1 <sup>st</sup> use | 82            |
| 2     | 2 <sup>nd</sup> use | 78            |
| 3     | 3 <sup>rd</sup> use | 72*           |

3<sup>rd</sup> run using recycled catalyst after 24 days.

#### FRIDEL-CRAFTS REACTION:

In Friedel-Crafts reaction, benzylation of anisoles is catalysed by copper triflate in  $\text{bmimBF}_4$ . Methoxybenzophenone is quantitatively obtained within

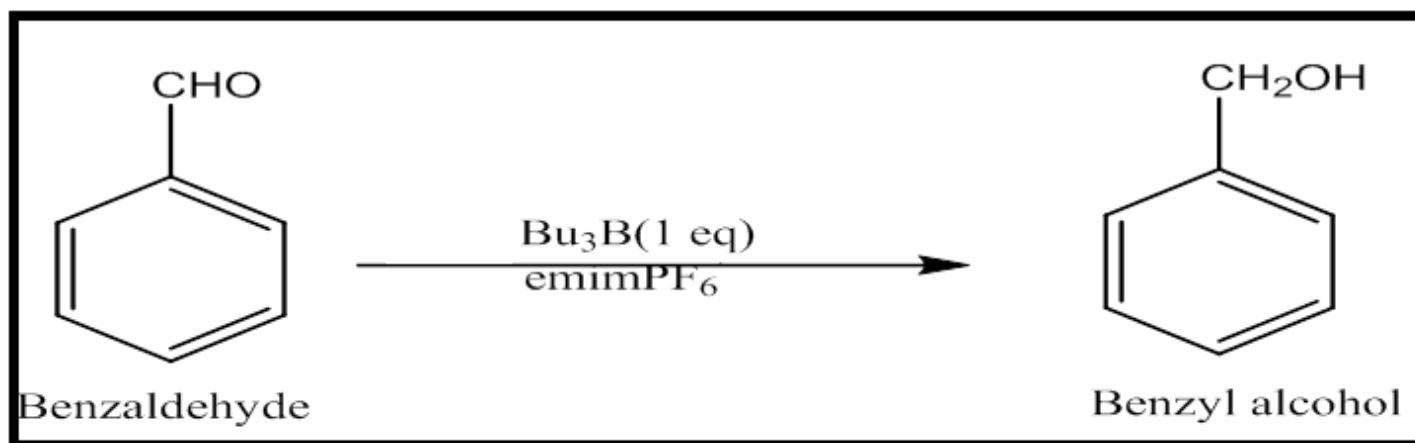
1hr, with p/o product ratio of 96/4<sup>[8]</sup>. The same reaction performed using Acetonitrile gave a lower conversion of 64% at 1hr with reduced p/o product ratio of 93/7<sup>[12]</sup>.



#### REDUCTION:

Reduction of aldehydes using trialkylboranes is an important organic transformation reaction. But reduction using simple trialkylboranes generally requires reaction temperatures above 150°C. kalbaka et al have reported this reduction using trialkylborane in which  $\text{bmimBF}_4$ ,  $\text{enimBF}_4$  and 1-ethyl-3-methylimidazolium hexafluorophosphate ( $\text{emimPF}_6$ ) are used as solvents<sup>13</sup> for example when

benzaldehyde was reduced by tributylborane in  $\text{emimPF}_6$ , the reaction proceeded rapidly at 100°C to give the product in high yield. Although long reaction time(48 hrs) is needed comparatively, the product can be obtained even at room temperature. In addition photoreduction has also been reported using ionic liquids<sup>14</sup>.



| Ionic liquid         | Temp (°C) | Time in hrs | Yield (%) |
|----------------------|-----------|-------------|-----------|
| bmim BF <sub>4</sub> | 100       | 16          | 93        |
| emim BF <sub>4</sub> | 100       | 16          | 90        |
| emim PF <sub>6</sub> | 100       | 16          | 96        |
| emim PF <sub>6</sub> | r.t.      | 48          | 94        |

r.t.: room temperature

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