# Ionic liquid based-alkylammonium cations: analysis of their behavior as nucleophile and acid catalyst in reactive systems

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**Abstract.** The investigation on ionic liquids (Lis) is growing, nevertheless many of their results are being reviewed. Our interest is to analyze the behavior of Lis alkylammonium derivatives in cycloaddition reactions analyzing their participation as catalyst and potential nucleophilic generated in situ.

**Keywords.** Ionic liquids, alkylammonium, catalyst

## Introduction

The studies on ionic liquids (ILs) are expanding and constant review. These liquids have new applications and benefits and they are published every year in varied areas of science. They differ from molten salts because they have a melting point below 100°C thus, we can find ILs solid at room temperature.

RTILs have attracted considerable attention because they are expected to be ideal solvents to provide novel reactions in green chemistry. The interest in this class of molecules arises from their use as liquid media for a variety of chemical transformations specially as substitutes of organic molecular solvents.

RTILs exhibit a variety of desirable properties, such as negligible vapour pressure, which makes them interesting for various applications. In particular, the option of fine-tuning

chemical and physical properties by an appropriate choice of cations and anions has stimulated much of the current excitement with respect to these compounds and has led to the term ‘design solvents’. As a consequence, the characterization of the properties of different clases of ILs used as solvent for specific applications and for chemical reactions and catalysis, has been intensively investigated.
Los protic ionic liquid (PILs) are considered a subset of ILs, they have a an available proton on the catión and this key feature, leading to numerous applications including in organic and inorganic synthesis, biological applications, electrochemical applications, lubrication, and as amphiphile self-assembly media. The ethylammonium nitrate (EAN) is the most studied however this, new applications are reported.

The Diels- Alder (DA) reaction is the most important because it is a key step in the synthesis of many natural products and pharmaceutical compounds. One key feature is its pronunced solvent dependence. The DA reaction between cyclopentadiene and acrolein was performed in ILs, was reported an increase on the chemical rate constant when was changed from non-polar (e.g. hexane) to polar ILs (e.g. [Hbim][N(Tf)2]). This is a clear evidence that the hydrogen bond in ionic liquids affect the reaction rate.

In previous work we presented the effect of molecular solvents on the hydrogen bonding present in PILs based-alkylammonium cations derivates of primary, secondary and tertiary amines. We determinate the pKa value of this PILs from Reichardt´s dye. We observed that for all PILs analysed the molecular solvent dimethyl sulfoxide (DMSO) increased the pKa values, indicating a strong catión-anion interaction and more basic nature of the PILs. Contrary, a molecular solvent as methanol or acetonitrile (AN) with characteristic hydrogen bond donor (HBD), turns these PILs more acidic.[i] Based on the above, is the most interest, analyse how behaviour the PILs based-alkylammonium cations on the DA reacción. We are looking for the improve in the conditions and times of reaction.[1]

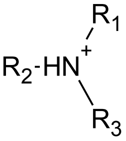
The aim of the present work is completing the studies about DA transformations developed in ionic liquids as reaction media employed substituted aromatic heterocycles with electron-withdrawing as electrophiles applying greener technology.[2]

Important issue in green chemistry is the use of organic solvents, considering that, usually DA transformations developed in molecular solvents require harsh conditions (high temperatures and pressures) and long reaction times, has risen to the occasion and is making substantial progress in replacing traditional processes with greener, more sustainable alternatives, though there is much still to do.

With this purpose, ammoniumn based ILs have been selected because they present differences in their HBD acidity. In general, our intention is showing the effect of bond-H in these reactions.

## Results and Discussion

The study of DA reactions was carried out employing 1-tosyl-2-nitropirrole **1a** as electrophilic dienophile, whereas 2-methyl-1,3-butadiene **2** was chosen as diene partner. The ionic liquids employed in the diverse cycloaddition reactions were: ethylammoniun nitrate (EAN), diethylammonium nitrate (DEAN) and triethylammonium nitrate (TEAN) (Scheme 1).



| Cation | Anion |
|---|---|
| $R_1$=$C_2H_5$; $R_2$=$R_3$=H (**EA**) | $NO_3^-$ |
| $R_1$= $R_2$=$C_2H_5$; $R_3$=H (**DEA**) | |
| $R_1$=$R_2$=$R_3$= $C_4H_9$ (**TBA**) | |

Scheme 1**.**

The reactions were development in a reactor at atmospheric pressure at 50 °|C for all PILs above mentioned in AN as molecular solvent. The reactions were checked by chromatographic methods each 4 h.

For EAN we detected at reaction time 4 h, a mixture of isomeric indoles **3a** and **3b** as the principal products with reasonable yield and dihydroindoles **4a** and **4b** (minority products). (Figure 1).

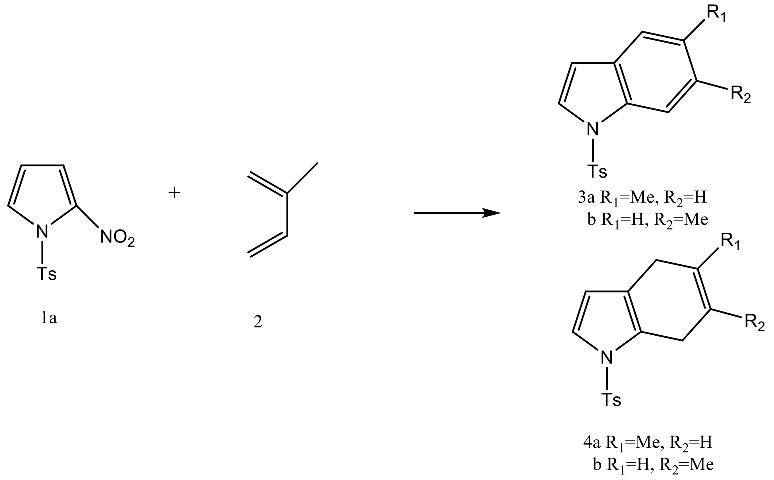


Figure 1

When DEAN was employed, the products were observed at reaction time 12 h instead, when TBAN was used, longer times are needed (28 h).

## Conclusions

It is possible design synthetic strategies greener with a right selection of PILs optimizing reaction times. The $pK_a$ values are similar for all PILs in AN, despite this, we can observe different times reaction. It is possible suppose that the PILs HBD characteristic influence in the bond-H network that this form. Thus, the reaction longer times for TBAN could be related with that the only hydrogen available is involved in the formation of this network.

## Acknowledgments

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