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Friedel–Crafts alkylation reactions in pyridinium-based ionic liquids

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Abstract

The Friedel–Crafts alkylations of benzene in pyridinium-based ionic liquids (ILs) were investigated. The effects of catalyst–IL composition, reactant composition, quantity of catalyst and reaction temperature on this reaction were studied. The reactions were found to proceed under mild conditions with conversion; a simple product isolation procedure was achieved. The ILs rendered this reaction green characteristics. The ILs could also be recycled and reused as opposed to traditional solvent–catalyst systems.

Keywords: Pyridinium-based ionic liquids; Alkylation; Friedel–Crafts; Iron chloride; Aluminum chloride

1. Introduction

Friedel–Crafts chemistry is of major importance both on laboratory and industrial scale. Research in this field is permanently ongoing and of high interest [1–5]. Alkylation of benzene with alkyl halides in the presence of aluminum chloride originally discovered by Charles Friedel and James M. Crafts in 1877, can be promoted by other Lewis acids, such as BF_3, $ZnCl_2$, $TiCl_4$, SbF_5, etc. The general mechanism of alkylation is shown in Scheme 1 [6].

The overall transformation of Friedel–Crafts alkylation introduces an alkyl group on an aromatic ring. Therefore, in industrial processes catalytic alkylation with alkenes is applied. However, the process has some disadvantages, such as long reaction time, formation of aluminate waste, troublesome product recovery and purification, and catalysts cannot be reused.

Recently, much attention has been focused on the use of ionic liquids as reaction media for various organic reactions, such as hydrogenation [7], oxidation [8], Diels–Alder reaction [9], Trost–Tsuji coupling [10], esterification [11], Beckman rearrangement [12], and others [13–16]. The ionic liquids are considered environmentally friendly or “green” media due to their favorable properties [17], such as chemical and thermal stability, no measurable vapor pressure, nonflammability, high ionic conductivity, also they are strongly solvating but non-coordinating. They have a profound effect on the activity and selectivity in reactions and in some cases, facilitate the isolation of products. They can be recycled and reused in most cases. All of these properties indicate that ILs may substitute volatile organic solvents.

There have been some reports on synthesis and improved reaction characteristics of the Friedel–Crafts reactions in ILs [18–22]. However, all these studies have focused only on the ILs derived from imidazole. Based on our earlier success, using pyridinium-based ionic liquids [23–25], herein, we report the application of these ionic liquids in the Friedel–Crafts alkylation.

2. Experimental

2.1. Synthesis of ionic liquids

Two ionic liquids, 1-ethyl-pyridinium trifluoroacetate ($[EtPy]^+[CF_3COO]^-$) and 1-ethyl-pyridinium tetrafluoroborate ($[EtPy]^+[BF_4]^-$), were employed in our study (Fig. 1).

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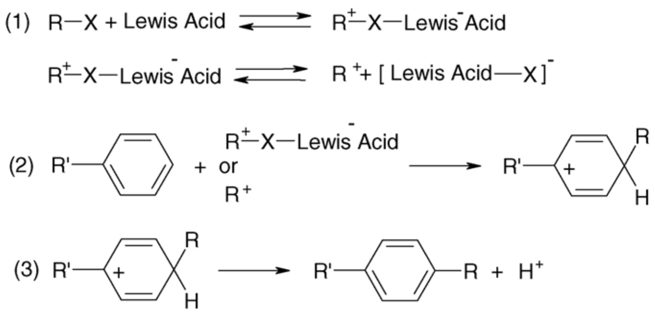


Scheme 1. General mechanism of alkylations.

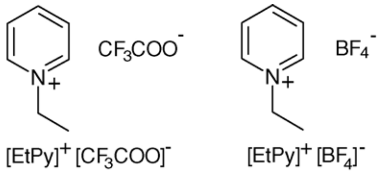


Fig. 1. Pyridinium-based ionic liquids.

These ILs were prepared following the literature method [26,27].

A general synthetic procedure could be described as follows: trifluoroacetic acid or tetrafluoroboric acid (0.2 mol) were slowly added to a stirred slurry of silver(I) oxide (0.1 mol) and distilled water (50 ml). To avoid photodegradation of silver(I) oxide, the reaction mixture was fully covered with aluminum foil. The reaction mixture was stirred continuously until the reaction was complete, which was indicated by the formation of a solution. A solution of *N*-ethyl-pyridinium bromide (0.2 mol) was added to the reaction mixture. As reaction took place and ILs formed, a yellow precipitate of silver(I) bromide started to be observed. The mixture was stirred at room temperature for a certain time until no more precipitate formed. The precipitate of silver(I) bromide was filtered off, and then the solvent was removed by rotary evaporation under vacuum at about 65 °C. The resulting ionic liquids were put in an oven overnight at 65 °C to remove the moisture.

2.2. Alkylation of benzene

The utility of ionic liquids $[EtPy]^+[CF_3COO]^-$ and $[EtPy]^+[BF_4]^-$ was investigated in alkylation of benzene (**1**) with 1-bromopropane (**2**), 1-chlorobutane (**3**) and benzyl chloride (**4**) (Scheme 2). The ILs were applied as such and with aluminum or iron chloride added.

In a typical reaction [28], the specified amount of catalyst (anhydrous $FeCl_3$ or $AlCl_3$) was added to pyridinium-based ionic liquid, and the mixture continuously stirred at 45 °C until the catalyst completely dissolved. Benzene (**1**) and alkyl halides (**2**, **3**, **4**) were directly added to the catalyst–IL solution. Two phases, i.e. ionic liquid and organic were formed and the mixture was stirred (250 rpm) at the desired reaction temperature for 4 h. The molar ratio of benzene:alkyl halide:ionic liquid was maintained at 2:1:1. At the end of the reaction, the organic layer could be easily decanted from the catalyst–IL system, and any organic residues were removed by extraction with diethylether.

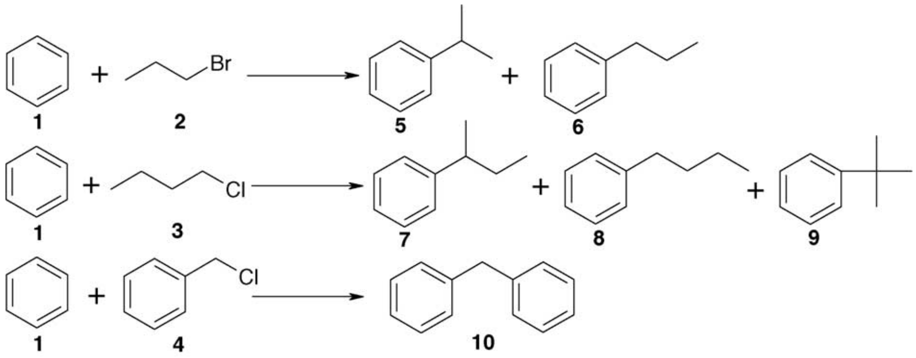
2.3. Analytical method

The reaction samples and products were analyzed using a Varian CP-3800 Gas Chromatograph equipped with SPB^{TM}-5 column, 30 m × 0.25 mm × 0.25 μm.

3. Results and discussion

3.1. Alkylation of benzene with 1-bromopropane

As shown in Scheme 2 Eq. (1), both *iso*-product (**5**) and *n*-product (**6**) were obtained in the alkylation of benzene and 1-bromopropane. Since the reaction proceeds via formation of a carbocation intermediate, this may undergo a hydride shift to form a more stable cation. In reactions with 1-bromopropane, the primary propyl cation undergoes a hydride shift to form the more stable isopropyl cation. Therefore, major product in each case is isopropylbenzene. Table 1 shows the results of reaction of benzene with 1-bromopropane in different catalyst–IL system at room temperature and at 50 °C.



Scheme 2. Friedel–Crafts alkylation reactions with benzene.