Preparation of aryl allyl ether in the recyclable ionic liquid [bmim]PF_6

Mei-Yun Zhou and Yi-Qun Li*

Department of Chemistry, Jinan University, Guangzhou 510632, P.R. China

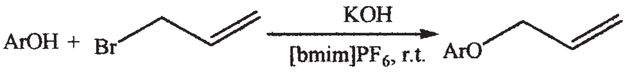
The recyclable room temperature ionic liquid [bmim]PF_6, namely l-butyl-3-methyl-imidazolium hexafluorophosphate, is used as an alternative solvent to dipolar aprotic solvents for the synthesis of aryl allyl ether by the Williamson method.

Keywords: aryl allyl ether, ionic liquid, preparation

Ionic liquids, especially imidazonium salts, have recently gained recognition as possible environmentally benign alternative chemical process solvents. This is mainly due to their nonvolatile nature, insolubility in some solvents as well as their ability to dissolve a wide range of organic and inorganic materials, allowing easy recovery of the ionic liquids and recycling. Examples of their application in organic reactions have been summarised elsewhere.[1]

Aryl allyl ether is very useful intermediate in organic synthesis. The Williamson reaction is a well known method for the preparation ethers. However, the reaction of alkylating agents with the phenoxide ions is conventionally carried out in organic solvents. The usual solvents for this type of reaction are DCM,[2] DMSO,[3] DMF,[4] CH_3CN,[5] *etc.* With the current desire to avoid the use of organic molecular solvents in organic synthesis, we decided to investigate the use of ionic liquids as alternative solvents for the Williamson reaction to prepare aryl allyl ethers. The ionic liquid employed here was the moisture stable l-butyl-3-methylimidazolium hexafluorophosphate [bmim]PF_6.[6] The ionic liquid is non-volatile, thermally stable, and depending on the anion, can present low solubility in water, alkanes and dialky ethers. We have now found that aryl allyl ethers can be obtained from various phenols and allyl bromide in the presence of potassium hydroxide in [bmim]PF_6 as a replacement for classical organic solvents at the ambient temperature.

The results are shown in Scheme 1.

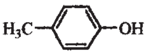
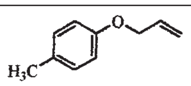
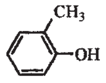
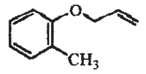
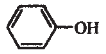
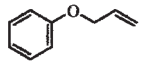
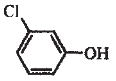
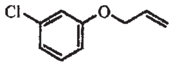
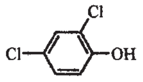
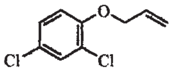
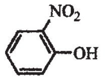
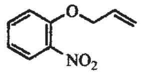
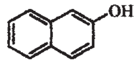
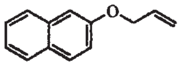


1 2

Scheme 1 The reaction of phenols with allyl bromide in [bmim]PF_6.

The reaction were carried out by simply mixing the phenol with the ally bromide and potassium hydroxide in [bmim]PF_6 and stirred at room temperature for 4h. The results are summarised in Table 1.

Table 1 The reaction of phenols with allyl bromide in [bmim]PF_6 at the ambient temperature

Entry	ArOH (**1**)	Products (**2**)[a]	Yield/%[b]
1			80.0
2			80
3			98 (96)[c]
4			96
5			98
6			82
7			91

[a]All product compared with the authentic samples and identified by GC/MS. [b]Yields of isolated products. [c]Data in parenthesis is the yield obtained from the fifth run of the recovery ionic liquid.

Upon completion of the reaction, the ionic liquid was almost quantitatively recovered by simple extraction of products with diethyl ether and removal of the unreacted inorganic salt and the inorganic by-product formed in the reaction with water. The recovered ionic liquid can be reused, after drying in a vacuum, without lost any activity.

In conclusion, the Williamson reaction can be successfully conducted in the ionic liquid [bmim]PF_6 with a number of advantages: the procedure is simple, the reaction condition is mild and the yields are excellent. Moreover, the reaction media can be reused.

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* Correspondence. E-mail: tlyq@jnu.edu.cn