



N-Substituted 3,4-dihydroisoquinolinium ionic liquids as catalysts in alkenes epoxidation reactions

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ABSTRACT

Because of their high reactivity, epoxides are one of the most important groups of organic compounds. These substances are synthesised primarily by the catalytic oxidation of alkenes in the liquid or gaseous phase. This study investigated new catalytic systems for epoxidation reactions using functionalised ionic liquids. These ionic liquids serve as oxygen transfer agents during the reactions. Several *N*-substituted 3,4-dihydroisoquinolinium ionic liquids were synthesised, and their potential as catalysts for epoxidation reactions was investigated. Cyclic alkenes such as cyclohexene and cyclooctene were used as model olefins.

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1. Introduction

The epoxidation of carbon–carbon double bonds is one of the most important reactions in organic chemistry. These reactions can be performed using different types of catalysts, including compounds and complexes that contain transition metals [1]. In addition, epoxidation reactions that use organic oxygen transfer agents are interesting. These oxygen transfer agents include ketones [2,3] and iminium salts [4]. The mechanism of the reaction with iminium salts is shown in Fig. 1 [5].

Epoxidation involves the initial transfer of an oxygen atom from the oxidising agent to the carbon–nitrogen double bond of the iminium group, forming the intermediate oxaziridinium salt [6]. This first step is followed by the transfer of the oxygen atom to the carbon–carbon double bond of the olefin. In this mechanism, the iminium salt acts as the oxygen transfer agent [7,8].

In practice, the following salts are most often used: *N*-substituted derivatives of isoquinoline [9,10], derivatives of binaphthalene [9,10] and pyrrolidine [4,10] (Fig. 2).

These iminium salts are obtained via the condensation of the corresponding aldehyde with a primary amine in the presence of an acid catalyst [6,10]. Isoquinolinium salts are obtained via the oxidation and alkylation of 1,2,3,4-tetrahydroisoquinoline [5]. Pyrrolidine derivatives are obtained via the reaction of *N*-trimethylsilylpyrrolidine with aromatic aldehydes [4].

In recent years, ionic liquids have become particularly attractive because of their physicochemical properties. One of the many interesting areas of study for these compounds is chemical synthesis, in which these compounds can act as auxiliary substances, such as solvents, extractants and catalysts [11]. Therefore, the synthesis of ionic liquids with an iminium functional group in the molecule and the potential uses of these ionic liquids in novel and practical catalytic systems for epoxidation are of interest. In addition to their catalytic properties in epoxidation reactions, these substances also possess the other advantages of ionic liquids. We conducted a study on the preparation of specific *N*-substituted 3,4-dihydroisoquinolinium ionic liquids, denoted by the general abbreviation [RDHQM][X], and subsequently investigated the use of these compounds as catalysts in epoxidation reactions.

2. Experimental

2.1. Preparation of 2-(2-bromoethyl)benzaldehyde

Preparation of 2-(2-bromoethyl)benzaldehyde is described by Crosthwaite et al. in [13]. The synthesis was started from 8.0 g (0.06 mol) of isochroman. A 40% aqueous solution of HBr (18 ml, 2.0 equiv. mol) was added to the crude 1-bromoisochroman. Crude 2-(2-bromoethyl)benzaldehyde was obtained as a red oil (15.35 g of approx. 75% purity).

2-(2-Bromoethyl)benzaldehyde 2. ¹H NMR δ_H (300 MHz, CDCl₃; TMS); 3.55–3.64 (4H, m, PhCH₂CH₂Br), 10.14 (1H, s, PhCHO)

isochroman 1. ¹H NMR δ_H (300 MHz, CDCl₃; TMS); 3.04 (2H, t, J 5.7 Hz, PhCH₂CH₂O), 4.77 (2H, s, PhCH₂O)

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