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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.

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. ^{1}H NMR δ_H (300 MHz, CDCl$_3$; TMS); 3.55–3.64 (4H, m, PhC$\underline{H_2}$C$\underline{H_2}$Br), 10.14 (1H, s, PhC$\underline{H}$O)

isochroman 1. ^{1}H NMR δ_H (300 MHz, CDCl$_3$; TMS); 3.04 (2H, t, J 5.7 Hz, PhCH$_2$C$\underline{H_2}$O), 4.77 (2H, s, PhC$\underline{H_2}$O)

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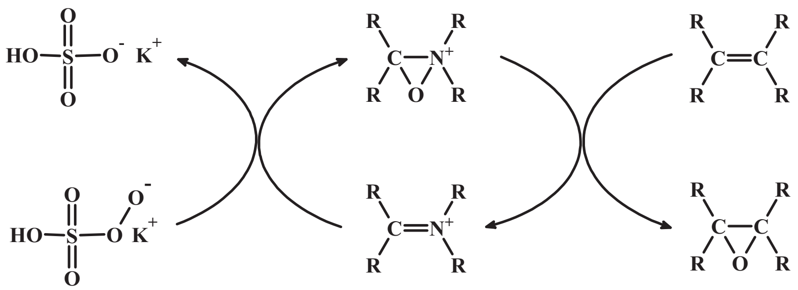

Fig. 1. The mechanism of olefin epoxidation reactions using iminium salts as catalysts.

2.2. General procedure for the preparation of N-substituted 3,4-dihydroisoquinolinium ionic liquids

General procedure for the preparation of *N*-substituted 3,4-dihydroisoquinoline derivatives is described also by Crosthwaite et al. in [13]. Solution of MX salt containing the desired anion (1.1 equiv. mol) in a minimal amount of acetonitrile, methanol, water or a mixture of these solvents, was added. This mixture was stirred for 10–60 min. After the reaction was complete, the solvent was removed under vacuum, which resulted in the crystallisation of the by-product, an inorganic salt. The contents of the flask were diluted with methylene chloride, and the mixture was filtered to remove the inorganic by-product. The filtrate containing the unreacted 2-(2-bromoethyl)benzaldehyde was concentrated on a rotary evaporator and transferred onto a chromatographic column filled with silica gel. The aldehyde was eluted with methylene chloride. After the elution of the aldehyde was complete, the ionic liquid was eluted with methanol. The methanol was removed using a rotary evaporator under high vacuum and a temperature of 70–80 °C for a few hours. The finished product was analysed by ^1H and ^{13}C NMR, Mass Spectroscopy and elemental analysis. The melting points of the solid products were determined.

The unreacted 2-(2-bromoethyl)benzaldehyde could be removed from the crude product by dissolving the material in methanol and adding a saturated aqueous sodium hydrogen sulphate(IV) solution. The sodium hydrogen sulphate forms a solid adduct with the aldehyde, which can be removed by vacuum filtration. The filtrate was concentrated with a rotary evaporator whilst maintaining the vacuum at a temperature of 70–80 °C for a few hours.

***N*-Butyl-3,4-dihydroisoquinolinium bromide [BDHQM][Br] 3a**. ^1H NMR (300 MHz, $CDCl_3$; TMS): δ_H/ppm = 0.96 (3H, t, J 7.5 Hz, $N{-}(CH_2)_3C\underline{H_3}$), 1.41 (2H, m, J 7.5 Hz, $N{-}(CH_2)_2C\underline{H_2}CH_3$), 1.89 (2H, m, J 7.5 Hz, $N{-}CH_2C\underline{H_2}CH_2CH_3$), 3.28 (2H, t, J 8.1 Hz, ${-}C\underline{H_2}CH_2N$), 4.06 (2H, t, J 7.8 Hz, ${-}CH_2C\underline{H_2}N$), 4.20 (2H, t, J 7.5 Hz, ${-}C\underline{H_2}(CH_2)_2CH_3$), 7.29–8.11 (4H, m, ${-}C_6\underline{H_4}{-}$), 10.27 (1H, s, ${-}C\underline{H}{=}N$). ^{13}C NMR (75 MHz, $CDCl_3$; TMS): δ_C/ppm = 13.97, 19.45, 25.15, 29.61 ($CH_3CH_2CH_2CH_2{-}$); 48.70, 60.02 (${-}CH_2CH_2N{-}$); 124.39, 128.00, 128.45, 134.55, 135.93, 137.84 (${-}C_6H_4{-}$); 166.09 ($HC{=}N{-}$). MS EI (70 eV) *m*/*z*: 188 (100%) $[C_9H_9N{-}C_4H_9]^+$, 130 (44%) $[C_9H_8N]^+$. Elemental analysis: found: C, 57.4; H, 7.00; N, 4.5%; Calc. for $C_{13}H_{18}NBr$: C, 58.2; H, 6.8; N, 5.2%. Density at 20 °C: 1.40 g cm^{-3}.

***N*-Butyl-3,4-dihydroisoquinolinium tetrafluoroborate $[BDHQM][BF_4]$ 3b**. ^1H NMR (300 MHz, $CDCl_3$; TMS): δ_H/ppm = 0.97 (3H, t, J 7.5 Hz, $N{-}(CH_2)_3C\underline{H_3}$), 1.43 (2H, m, J 7.5 Hz, $N{-}(CH_2)_2C\underline{H_2}CH_3$), 1.90 (2H, m, J 7.5 Hz, $N{-}CH_2C\underline{H_2}CH_2CH_3$), 3.31 (2H, t, J 8.1 Hz, ${-}C\underline{H_2}CH_2N$), 4.09 (2H, t, J 7.8 Hz, ${-}CH_2C\underline{H_2}N$), 4.22 (2H, t, J 7.5 Hz, $N{-}C\underline{H_2}(CH_2)_2CH_3$), 7.29–7.72 (4H, m, ${-}C_6\underline{H_4}{-}$), 9.76 (1H, s, ${-}C\underline{H}{=}N$). ^{13}C NMR (75 MHz, $CDCl_3$; TMS): δ_C/ppm = 13.26, 19.22, 25.07, 29.13 ($CH_3CH_2CH_2CH_2{-}$); 48.21, 60.53 (${-}CH_2CH_2N{-}$); 124.31, 127.96, 128.39, 134.23, 135.80, 137.82 (${-}C_6H_4{-}$); 166.35 ($HC{=}N{-}$). MS EI (70 eV) *m*/*z*: 188 (100%) $[C_9H_9N{-}C_4H_9]^+$, 130 (58%) $[C_9H_8N]^+$. Elemental Analysis: Found: C, 55.3; H, 7.0; N, 4.55%; Calc. for $C_{13}H_{18}NBF_4$: C, 56.75; H, 6.6; N, 5.1%. mp 43.2–47.3 °C (measured by DSC).

***N*-Butyl-3,4-dihydroisoquinolinium bis(trifluoromethanesulfonyl)imide $[BDHQM][NTf_2]$ 3c**. ^1H NMR (300 MHz, $CDCl_3$; TMS): δ_H/ppm = 1.00 (3H, t, J 7.5 Hz, $N{-}(CH_2)_3C\underline{H_3}$), 1.44 (2H, m, J 7.8 Hz, $N{-}(CH_2)_2C\underline{H_2}CH_3$), 1.89 (2H, m, J 7.5 Hz, $N{-}CH_2C\underline{H_2}CH_2CH_3$), 3.29 (2H, t, J 8.1 Hz, ${-}C\underline{H_2}CH_2N$), 4.04 (4H, t, J 7.8 Hz, ${-}CH_2C\underline{H_2}N$, $N{-}C\underline{H_2}(CH_2)_2CH_3$), 7.26–7.85 (4H, m, ${-}C_6\underline{H_4}{-}$), 8.86 (1H, s, ${-}C\underline{H}{=}N$). ^{13}C NMR (75 MHz, $CDCl_3$; TMS): δ_C/ppm = 13.28, 19.16, 25.15, 29.40 ($CH_3CH_2CH_2CH_2{-}$); 52.08, 61.22 (${-}CH_2CH_2N{-}$); 117.67, 121.91 ($N(SO_2CF_3)_2$); 124.12, 128.29, 128.99, 134.49, 135.72, 138.76 (${-}C_6H_4{-}$); 167.17 ($HC{=}N{-}$). MS EI (70 eV) *m*/*z*: 188 (100%) $[C_9H_9N{-}C_4H_9]^+$, 130 (51%) $[C_9H_8N]^+$. Elemental Analysis: Found: C, 38.3; H, 3.4; N, 5.6%; Calc. for $C_{15}H_{18}N_2O_4S_2F_6$: C, 38.45; H, 3.9; N, 6.0%. Density at 20 °C: 1.59 g cm^{-3}.

***N*-Hexyl-3,4-dihydroisoquinolinium bromide [HDHQM][Br] 4a**. ^1H NMR (300 MHz, $CDCl_3$; TMS): δ_H/ppm = 0.87 (3H, t, J 6.9 Hz, $N{-}(CH_2)_5C\underline{H_3}$), 1.26–1.44 (6H, m, J 7.8. Hz, $N{-}CH_2CH_2{-}(C\underline{H_2})_{\underline{3}}{-}CH_3$), 1.93 (2H, m, J 6.9 Hz, $N{-}CH_2{-}C\underline{H_2}{-}(CH_2)_3CH_3$), 3.36 (2H, t, J 8.1 Hz, ${-}C\underline{H_2}CH_2N$), 4.15 (2H, t, J 7.8 Hz, ${-}CH_2C\underline{H_2}N$), 4.34 (2H, t, J 7.5 Hz, $N{-}C\underline{H_2}(CH_2)_4CH_3$), 7.32–8.16 (4H, m, ${-}C_6\underline{H_4}{-}$), 10.32 (1H, s, ${-}C\underline{H}{=}N$). ^{13}C NMR (75 MHz, $CDCl_3$; TMS): δ_C/ppm = 13.79, 22.21, 25.41, 25.74, 27.47; 31.02 ($CH_3CH_2CH_2CH_2CH_2CH_2{-}$); 48.39, 60.81 (${-}CH_2CH_2N{-}$); 124.47, 127.13, 128.43, 134.60, 135.70, 137.78 (${-}C_6H_4{-}$); 166.70 ($H_C{=}N{-}$). MS EI (70 eV) *m*/*z*: 216 (100%) $[C_9H_9N{-}C_6H_{13}]^+$, 130

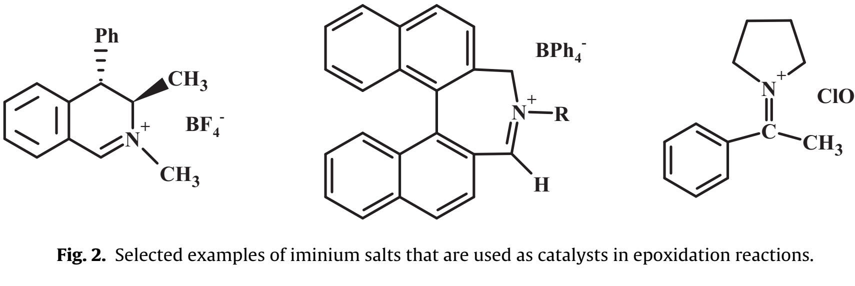

Fig. 2. Selected examples of iminium salts that are used as catalysts in epoxidation reactions.

(39%) $[C_9H_8N]^+$. Elemental Analysis: Found: C, 59.5; H, 7.4; N, 3.6%; Calc. for $C_{15}H_{22}NBr$: C, 60.8; H, 7.5; N, 4.7%. Density at 20 °C: 1.32 g cm^{-3}.

***N*-Hexyl-3,4-dihydroisoquinolinium tetrafluoroborate [HDHQM][BF$_4$] 4b**. ^{1}H NMR (300 MHz, $CDCl_3$; TMS): δ_H/ppm = 0.87 (3H, t, J 6.9 Hz, $N{-}(CH_2)_5C\underline{H_3}$), 1.25–1.42 (6H, m, J 7.8 Hz, $N{-}CH_2CH_2{-}(C\underline{H_2})_3{-}CH_3$), 1.91 (2H, m, J 6.9 Hz, $N{-}CH_2{-}C\underline{H_2}{-}(CH_2)_3CH_3$), 3.32 (2H, t, J 7.8 Hz, ${-}C\underline{H_2}CH_2N$), 4.11 (2H, t, J 8.1 Hz, ${-}CH_2C\underline{H_2}N$), 4.22 (2H, t, J 7.5 Hz, $N{-}C\underline{H_2}(CH_2)_4CH_3$), 7.33–8.05 (4H, m, ${-}C_6\underline{H_4}{-}$), 9.57 (1H, s, ${-}C\underline{H}{=}N$). ^{13}C NMR (75 MHz, $CDCl_3$; TMS): δ_C/ppm = 13.73, 22.16, 25.18, 25.66, 27.33, 30.92 ($CH_3CH_2CH_2CH_2CH_2CH_2{-}$); 48.26, 60.86 (${-}CH_2CH_2N{-}$); 124.39, 127.99, 128.38, 134.38, 135.81, 137.83 (${-}C_6H_4{-}$); 166.45 ($HC{=}N{-}$). MS EI (70 eV) *m/z*: 216 (100%) $[C_9H_9N{-}C_6H_{13}]^+$, 130 (51%) $[C_9H_8N]^+$. Elemental Analysis: Found: C, 58.2; H, 7.3; N, 4.2%; Calc. for $C_{15}H_{22}NBF_4$: C, 59.4; H, 7.3; N, 4.6%. Density at 20 °C: 1.48 g cm^{-3}.

***N*-Hexyl-3,4-dihydroisoquinolinium bis(trifluoromethanesulfonyl)imide [HDHQM][NTf$_2$] 4c**. ^{1}H NMR (300 MHz, CDCl3; TMS): δ_H/ppm = 0.88 (3H, t, J 6.9 Hz, $N{-}(CH_2)_5C\underline{H_3}$), 1.26–1.38 (6H, m, J 7.8 Hz, $N{-}CH_2CH_2{-}(C\underline{H_2})_3{-}CH_3$), 1.88 (2H, m, J 6.9 Hz, $N{-}CH_2{-}C\underline{H_2}{-}(CH_2)_3CH_3$), 3.26 (2H, t, J 7.8 Hz, ${-}C\underline{H_2}CH_2N$), 4.00 (4H, m, J 8.1 Hz, ${-}CH_2C\underline{H_2}N$, $N{-}C\underline{H_2}(CH_2)_4CH_3$), 7.35–7.82 (4H, m, ${-}C_6\underline{H_4}{-}$), 8.83 (1H, s,${-}C\underline{H}{=}N$). ^{13}C NMR (75 MHz, $CDCl_3$; TMS): δ_C/ppm = 13.69, 22.18, 25.02, 25.62, 27.34, 30.88 ($CH_3CH_2CH_2CH_2CH_2CH_2{-}$); 48.46, 61.29 (${-}CH_2CH_2N{-}$); 117.36, 121.61 ($N(SO_2CF_3)_2$); 124.08, 128.28, 128.76, 134.29, 135.88, 138.61 (${-}C_6H_4{-}$); 166.09 ($HC{=}N{-}$). MS EI (70 eV) *m/z*: 216 (100%) $[C_9H_9N{-}C_6H_{13}]^+$, 130 (31%) $[C_9H_8N]^+$. Elemental Analysis: Found: C, 40.7; H, 4.4; N, 5.0%; Calc. for $C_{17}H_{22}N_2O_4S_2F_6$: C, 41.1; H, 4.5; N, 5.6%. Density at 20 °C: 1.69 g cm^{-3}.

***N*-Octyl-3,4-dihydroisoquinolinium bromide [OcDHQM][Br] 5a**. ^{1}H NMR (300 MHz, $CDCl_3$; TMS): δ_H/ppm = .85 (3H, m, J 7.5 Hz, $N{-}(CH_2)_7C\underline{H_3}$), 1.21–1.32 (10H, m, J 7.8 Hz, $N{-}CH_2CH_2{-}(C\underline{H_2})_5{-}CH_3$), 1.93 (2H, m, J 7.2 Hz, $N{-}CH_2{-}C\underline{H_2}{-}(CH_2)_5CH_3$), 3.33 (2H, t, J 8.1 Hz, ${-}C\underline{H_2}CH_2N$), 4.15 (2H, t,J 7.2 Hz, ${-}CH_2C\underline{H_2}N$), 4.30 (2H, t, J 7.5 Hz, $N{-}C\underline{H_2}(CH_2)_6CH_3$), 7.26–8.11 (4H, m, ${-}C_6\underline{H_4}{-}$), 10.38 (1H, s, ${-}C\underline{H}{=}N$). ^{13}C NMR (75 MHz, $CDCl_3$; TMS): δ_C/ppm = 13.98, 22.50, 26.08, 26.60, 27.35, 28.89, 29.01, 31.64 ($CH_3(CH_2)_6CH_2{-}$); 50.46, 62.01 (${-}CH_2CH_2N{-}$); 126.48, 127.00, 127.34, 127.82, 129.95, 133.42 (${-}C_6H_4{-}$); 166.50 ($HC{=}N{-}$). MS EI (70 eV) *m/z*: 244 (37%) $[C_9H_9N{-}C_8H_{17}]^+$, 130 (49%) $[C_9H_8N]^+$. Elemental Analysis: Found: C, 64.0; H, 8.5; N, 4.2%; Calc. for $C_{17}H_{26}NBr$: C, 62.95; H, 8.1; N, 4.3%. Density at 20 °C: 1.45 g cm^{-3}.

***N*-Octyl-3,4-dihydroisoquinolinium tetrafluoroborate [OcDHQM][BF$_4$] 5b**. ^{1}H NMR (300 MHz, $CDCl_3$; TMS): δ_H/ppm = 0.86 (3H, m, J 6.9 Hz, $N{-}(CH_2)_7C\underline{H_3}$), 1.25–1.41 (10H, m, J 7.8 Hz, $N{-}CH_2CH_2{-}(C\underline{H_2})_5{-}CH3$), 1.90 (2H, m, J 6.9 Hz, $N{-}CH_2{-}C\underline{H_2}{-}(CH_2)_5CH_3$), 3.31 (2H, t, J 8.1 Hz, ${-}C\underline{H_2}CH_2N$), 4.09 (2H, t,J 8.1 Hz, ${-}CH_2C\underline{H_2}N$), 4.20 (2H, t, J 7.5 Hz, $N{-}C\underline{H_2}(CH_2)_6CH_3$), 7.21–8.16 (4H, m, ${-}C_6\underline{H_4}{-}$), 9.70 (1H, s, ${-}C\underline{H}{=}N$). ^{13}C NMR (75 MHz, $CDCl_3$; TMS): δ_C/ppm = 13.88, 22.44, 26.38, 27.19, 27.58, 28.81, 29.01, 31.59 ($CH_3(CH_2)_6CH_2{-}$); 50.00, 61.60 (${-}CH_2CH_2N{-}$); 124.50, 126.97, 127.51, 127.98, 130.11, 134.53 (${-}C_6H_4{-}$); 166.92 ($HC{=}N{-}$). MS EI (70 eV) *m/z*: 244 (23%) $[C_9H_9N{-}C_8H_{17}]^+$, 130 (43%) $[C_9H_8N]^+$. Elemental Analysis: Found: C, 62.3; H, 8.1; N, 4.35%; Calc. for $C_{17}H_{26}NBF_4$: C, 61.6; H, 7.9; N, 4.2%. Density at 20 °C: 1.38 g cm^{-3}.

***N*-Octyl-3,4-dihydroisoquinolinium bis(trifluoromethanesulfonyl)imide [OcDHQM][NTf$_2$] 5c**. ^{1}H NMR (300 MHz, $CDCl_3$; TMS): δ_H/ppm = 0.86 (3H, m, J 6.9 Hz, $N{-}(CH_2)_7C\underline{H_3}$), 1.19–1.27 (10H, m, J 7.8 Hz, $N{-}CH_2CH_2{-}(C\underline{H_2})_5{-}CH_3$), 1.63 (2H, m, J 6.9 Hz, $N{-}CH_2{-}C\underline{H_2}{-}(CH_2)_5CH_3$), 2.98 (2H, t, J 8.1 Hz, ${-}C\underline{H_2}CH_2N$), 4.01 (4H, m, J 8.1 Hz, ${-}CH_2C\underline{H_2}N$, $N{-}C\underline{H_2}(CH_2)_6CH_3$), 7.21–8.22 (4H, m, ${-}C_6\underline{H_4}{-}$), 8.80 (1H, s, ${-}C\underline{H}{=}N$). ^{13}C NMR (75 MHz, $CDCl_3$; TMS): δ_C/ppm = 13.85, 22.44, 25.93, 27.07, 27.40, 28.72, 28.79, 31.53 ($CH_3(CH_2)_6CH_2{-}$); 48.49, 61.33 (${-}CH_2CH_2N{-}$); 117.29, 121.54 ($N(SO_2CF_3)_2$); 124.05, 125.78, 128.34, 130.48, 134.25, 137.50 (${-}C_6H_4{-}$); 166.05 ($HC{=}N{-}$). MS EI (70 eV) *m/z*: 244 (34%) $[C_9H_9N{-}C_8H_{17}]^+$, 130 (26%) $[C_9H_8N]^+$. Elemental Analysis: Found: C, 42.3; H, 5.1; N, 5.3%; Calc. for $C_{19}H_{26}N_2O_4S_2F_6$: C, 43.5; H, 5.0; N, 5.3%. Density at 20 °C: 1.51 g cm^{-3}.

***N*-Dodecyl-3,4-dihydroisoquinolinium bromide [DodDHQM][Br] 6a**. ^{1}H NMR (300 MHz, $CDCl_3$; TMS): δ_H/ppm = 0.88 (3H, t, J 6.9 Hz, $N{-}(CH_2)_{11}C\underline{H_3}$), 1.24 (18H, m, J 6.9 Hz, $N{-}CH_2CH_2(C\underline{H_2})_9CH_3$), 1.93 (2H, m, J 6.9 Hz, $N{-}CH_2C\underline{H_2}(CH_2)_9CH_3$), 3.36 (2H, t, J 7.8 Hz, ${-}C\underline{H_2}CH_2N$), 4.15 (2H, t, J 8.1 Hz, ${-}CH_2C\underline{H_2}N$), 4.34 (2H, t, J 7.5 Hz, $N{-}C\underline{H_2}(CH_2)_{10}CH_3$), 7.34–8.16 (4H, m, ${-}C_6\underline{H_4}{-}$), 10.28 (1H, s, ${-}C\underline{H}{=}N$). ^{13}C NMR (75 MHz, $CDCl_3$; TMS): δ_C/ppm = 13.91, 22.45, 25.36, 26.08, 27.50, 28.94, 29.10, 29.19, 29.31, 29.39, 29.48, 31.67 ($CH_3(CH_2)_{10}CH_2{-}$); 48.34, 60.81 (${-}CH_2CH_2N{-}$); 124.44, 127.94, 128.37, 134.53, 135.69, 137.72 (${-}C_6H_4{-}$); 166.63 ($HC{=}N{-}$). MS EI (70 eV) *m/z*: 300 (85%) $[C_9H_9N{-}C_{12}H_{25}]^+$, 130 (100%) $[C_9H_8N]^+$. Elemental Analysis: Found: C, 64.6; H, 8.7; N, 3.9%; Calc. for $C_{21}H_{34}NBr$: C, 66.3; H, 9.0; N, 3.7%. mp 64.0–67.4 °C (measured by DSC).

***N*-Dodecyl-3,4-dihydroisoquinolinium tetrafluoroborate [DodDHQM][BF$_4$] 6b**. ^{1}H NMR (300 MHz, $CDCl_3$; TMS): δ_H/ppm = 0.86 (3H, t, J 6.9 Hz, $N{-}(CH_2)_{11}C\underline{H_3}$), 1.24 (18H, m, J 6.9 Hz, $N{-}CH_2CH_2(C\underline{H_2})_9CH_3$), 1.90 (2H, m, J 6.9 Hz, $N{-}CH_2C\underline{H_2}(CH_2)_9CH_3$), 3.31 (2H, t, J 7.8 Hz, ${-}C\underline{H_2}CH_2N$), 4.08 (2H, t,J 8.1 Hz, ${-}CH_2C\underline{H_2}N$), 4.18 (2H, t, J 7.5 Hz, $N{-}C\underline{H_2}(CH_2)_{10}CH_3$), 7.31–8.01 (4H, m, ${-}C_6\underline{H_4}{-}$), 9.57 (1H, s, ${-}C\underline{H}{=}N$). ^{13}C NMR (75 MHz, $CDCl_3$; TMS): δ_C/ppm = 13.99, 22.54, 25.19, 26.11, 27.46, 28.96, 29.20, 29.27, 29.39, 29.56, 29.55, 31.75 ($CH_3(CH_2)_{10}CH_2{-}$); 48.23, 61.00 (${-}CH_2CH_2N{-}$); 124.44, 128.02, 128.47, 134.43, 135.85, 137.90 (${-}C_6H_4{-}$); 166.48 ($HC{=}N{-}$). MS EI (70 eV) *m/z*: 300 (100%) $[C_9H_9N{-}C_{12}H_{25}]^+$, 130 (72%) $[C_9H_8N]^+$. Elemental Analysis: Found: C, 64.5; H, 8.9; N, 3.3%; Calc. for $C_{21}H_{34}NBF_4$: C, 65.1; H, 8.9; N, 3.6%. mp 58.0–60.3 °C (measured by DSC).

***N*-Dodecyl-3,4-dihydroisoquinolinium bis(trifluoromethanesulfonyl)imide [DodDHQM][NTf$_2$] 6c**. ^{1}H NMR (300 MHz, $CDCl_3$; TMS): δ_H/ppm = 0.87 (3H, t, J 6.6 Hz, $N{-}(CH_2)_{11}C\underline{H_3}$), 1.25 (18H, m, J 7.2 Hz, $N{-}CH_2CH_2(C\underline{H_2})_9CH_3$), 1.88 (2H, m, J 6.6 Hz, $N{-}CH_2C\underline{H_2}(CH_2)_9CH_3$), 3.27 (2H, t, J 8.1 Hz, ${-}C\underline{H_2}CH_2N$), 4.00 (4H, t, J 7.5 Hz, ${-}CH_2C\underline{H_2}N$, $N{-}C\underline{H_2}(CH_2)_{10}CH_3$), 7.38–7.81 (4H, m, ${-}C_6H_4{-}$), 8.79 (1H, s, ${-}C\underline{H}{=}N$). ^{13}C NMR (75 MHz, $CDCl_3$; TMS): δ_C/ppm = 14.05, 22.62, 25.04, 26.03, 27.44, 28.86, 29.24, 29.27, 29.39, 29.53, 29.61, 31.85 ($CH_3(CH_2)_{10}CH_2{-}$); 48.46, 61.39 (${-}CH_2CH_2N{-}$); 117.25, 121.49 ($N(SO_2CF_3)_2$); 124.03, 128.31, 128.85, 134.33, 135.82, 138.71 (${-}C_6H_4{-}$); 166.08 ($HC{=}N{-}$). MS EI (70 eV) *m/z*: 300 (100%) $[C_9H_9N{-}C_{12}H_{25}]^+$, 130 (20%) $[C_9H_8N]^+$. Elemental Analysis: Found: C, 48.8; H, 5.3; N, 4.2%; Calc. for $C_{23}H_{34}N_2O_4S_2F_6$: C, 47.6; H, 5.9; N, 4.8%. Density at 20 °C 1.60 g cm^{-3}.

***N-iso*-pentyl-3,4-dihydroisoquinolinium bromide [*i*-PDHQM][Br] 7a**. ^{1}H NMR (300 MHz, $CDCl_3$; TMS): δ_H/ppm = 0.86 (3H, q, J 6.9 Hz, $N{-}(CH_2)_2CH(C\underline{H_3})_2)$), 1.00 (3H, q, J 6.9 Hz, $N{-}(CH_2)_2CH(C\underline{H_3})_2)$, 1.71 (2H, q, J 6.9 Hz, $N{-}CH_2{-}C\underline{H_2}{-}CH(CH_3)_2)$, 1.85 (1H, m, J 6.9 Hz, $N{-}(CH_2)_2{-}C\underline{H}{-}(CH_3)_2)$, 3.38 (2H, t, J 7.8 Hz, ${-}C\underline{H_2}CH_2N$), 4.18 (2H, t, J 7.8 Hz, ${-}CH_2C\underline{H_2}N$), 4.32 (2H, t, J 7.8 Hz, $N{-}C\underline{H_2}{-}CH_2CH(CH_3)_2)$, 7.33–8.12 (4H, m, ${-}C_6\underline{H_4}{-}$), 10.36 (1H, s, ${-}C\underline{H}{=}N$). ^{13}C NMR (75 MHz, $CDCl_3$; TMS): δ_C/ppm = 22.13, 26.76, 28.81, 31.46 ($(CH_3)_2CHCH_2CH_2{-}$); 50.00, 63.20 (${-}CH_2CH_2N{-}$); 125.93, 126.63, 128.40, 131.11, 136.58, 137.70 (${-}C_6H_4{-}$); 170.11 ($HC{=}N{-}$). MS EI (70 eV) *m/z*: 202 (19%) $[C_9H_9N\text{-}CH_2CH_2CH(CH_3)_2]^+$, 130 (39%) $[C_9H_8N]^+$. Elemental

Analysis: Found: C, 60.4; H, 7.6; N, 4.5%; Calc. for $C_{14}H_{20}NBr$: C, 59.6; H, 7.2; N, 5.0%. Density at 20 °C: 1.63 g cm^{-3}.

***N-iso*-pentyl-3,4-dihydroisoquinolinium tetrafluoroborate [*i*-PDHQM][BF$_4$] 7b**. ^{1}H NMR (300 MHz, $CDCl_3$; TMS): δ_H/ppm = 0.96 (6H, m, J 6.9 Hz, $N{-}(CH_2)_2CH(C\underline{H_3})_{\underline{2}}$), 1.68 (2H, q, J 6.9 Hz, $N{-}CH_2{-}C\underline{H_2}{-}CH(CH_3)_2$), 1.78 (1H, m, J 6.9 Hz, $N{-}(CH_2)_2{-}C\underline{H}{-}(CH_3)_2$), 3.37 (2H, t, J 7.8 Hz, $-C\underline{H_2}CH_2N$), 4.04 (2H, t, J 7.8 Hz, $-CH_2C\underline{H_2}N$), 4.50 (2H, t, J 7.8 Hz, $N{-}C\underline{H_2}{-}CH_2CH(CH_3)_2$), 7.39–8.08 (4H, m, $-C_6\underline{H_4}-$), 9.70 (1H, s, $-C\underline{H}{=}N$). ^{13}C NMR (75 MHz, $CDCl_3$; TMS): δ_C/ppm = 21.82, 25.91, 27.53, 31.91 ($(CH_3)_2CHCH_2CH_2-$); 48.87, 59.98 ($-CH_2CH_2N-$); 124.18, 125.90, 127.80, 130.47, 135.71, 137.66 ($-C_6H_4-$); 166.04 ($HC{=}N-$). MS EI (70 eV) *m*/*z*: 202 (16%) $[C_9H_9N{-}CH_2CH_2CH(CH_3)_2]^+$, 130 (37%) $[C_9H_8N]^+$. Elemental Analysis: Found: C, 58.1; H, 6.9; N, 4.3%; Calc. for $C_{14}H_{20}NBF_4$: C, 58.15; H, 7.0; N, 4.85%. Density at 20 °C: 1.43 g cm^{-3}.

***N-iso*-pentyl-3,4-dihydroisoquinolinium bis(trifluoromethanesulfonyl)imide [*i*-PDHQM][NTf$_2$] 7c**. ^{1}H NMR (300 MHz, CDCl3; TMS): δH/ppm = 0.97 (6H, d, J 6.5 Hz, $N{-}(CH_2)_2CH(C\underline{H_3})_{\underline{2}}$), 1.70 (2H, q, J 6.6 Hz, $N{-}CH_2{-}C\underline{H_2}{-}CH(CH_3)_2$), 1.81 (1H, m, J 6.6 Hz, $N{-}(CH_2)_2{-}C\underline{H}{-}(CH_3)_2$), 3.27 (2H, t, J 7.8 Hz, $-C\underline{H_2}CH_2N$), 4.02 (4H, t, J 7.8 Hz, $-CH_2C\underline{H_2}N$, $N{-}C\underline{H_2}{-}CH_2CH(CH_3)_2$), 7.27–8.06 (4H, m, $-C_6\underline{H_4}-$), 8.89 (1H, s, $-C\underline{H}{=}N$). ^{13}C NMR (75 MHz, $CDCl_3$; TMS): δ_C/ppm = 21.89, 25.03, 27.64, 35.98 ($(CH_3)_2CHCH_2CH_2-$); 48.57, 59.83, ($-CH_2CH_2N-$); 117.54, 121.80 ($N(SO_2CF_3)_2$); 124.17, 125.65, 127.60, 130.15, 135.87, 138.44 ($-C_6H_4-$); 166.08 ($HC{=}N-$). MS EI (70 eV) *m*/*z*: 202 (43%) $[C_9H_9N{-}CH_2CH_2CH(CH_3)_2]^+$, 130 $[C_9H_8N]^+$ (100%). Elemental Analysis: Found: C, 38.35; H, 3.7; N, 4.7%; Calc. for $C_{16}H_{20}N_2O_4S_2F_6$: C, 39.8; H, 4.2; N, 5.8%. Density at 20 °C: 1.62 g cm^{-3}.

***N*-Cyclohexyl-3,4-dihydroisoquinolinium bromide [cHDHQM][Br] 8a**. ^{1}H NMR (300 MHz, $CDCl_3$; TMS): δ_H/ppm = 1.28–2.23 (10H, m, J 12.9 Hz, J 3.3 Hz, $N{-}CH(C\underline{H_2}C\underline{H_2})_{\underline{2}}C\underline{H_2}$), 3.33 (2H, t, J 7.8 Hz, $-C\underline{H_2}CH_2N$), 4.16 (2H, t, J 7.8 Hz, $-CH_2C\underline{H_2}N$), 4.47 (1H, m, J 11.7 Hz, J 3.3 Hz, $N{-}C\underline{H}(CH_2CH_2)_2CH_2$), 7.32–8.35 (4H, m, $-C_6\underline{H_4}-$), 10.30 (1H, s, $-C\underline{H}{=}N$). ^{13}C NMR (75 MHz, $CDCl_3$; TMS): δ_C/ppm = 24.39, 24.60, 25.63; 30.65 ($N{-}CH(CH_2CH_2)_2CH_2$); 46.56, 70.08 ($-CH_2CH_2N-$); 124.75, 127.80, 128.45, 135.05, 136.02, 137.69 ($-C_6H_4-$); 165.35 ($HC{=}N-$). MS EI (70 eV) *m*/*z*: 214 (69%) $[C_9H_9N{-}C_6H_{11}]^+$, 130 (100%) $[C_9H_8N]^+$. Elemental Analysis: Found: C, 61.0; H, 7.0; N, 4.3%; Calc. for $C_{15}H_{20}NBr$: C, 61.2; H, 6.9; N, 4.8%. mp 162.9–168.2 °C (measured by DSC).

***N*-Cyclohexyl-3,4-dihydroisoquinolinium tetrafluoroborate [cHDHQM][BF$_4$] 8b**. ^{1}H NMR (300 MHz, $CDCl_3$; TMS): δ_H/ppm = 1.26–2.20 (10H, m, J 12.9 Hz, J 3.3 Hz $N{-}CH(C\underline{H_2}C\underline{H_2})_{\underline{2}}C\underline{H_2}$), 3.29 (2H, t, J 7.8 Hz, $-C\underline{H_2}CH_2N$), 4.11 (2H, t, J 7.8 Hz, $-CH_2C\underline{H_2}N$), 4.28 (1H, m, J 11.7 Hz, J 3.6 Hz, $N{-}C\underline{H}(CH_2CH_2)_2CH_2$), 7.31–8.16 (4H, m, $-C_6H_4-$), 9.71 (1H, s, $-C\underline{H}{=}N$). ^{13}C NMR (75 MHz, $CDCl_3$; TMS): δ_C/ppm = 24.42, 24.65, 25.47; 30.57 ($N{-}CH(CH_2CH_2)_2CH_2$); 46.55, 70.30 ($-CH_2CH_2N-$); 124.67, 127.87, 128.50, 134.80, 136.20, 137.82 ($-C_6H_4-$); 165.16 ($HC{=}N-$). MS EI (70 eV) *m*/*z*: 214 (41%) $[C_9H_9N{-}C_6H_{11}]^+$, 130 (100%) $[C_9H_8N]^+$. Elemental Analysis: Found: C, 58.8; H, 6.7; N, 4.4%; Calc. for $C_{15}H_{20}NBF_4$: C, 59.8; H, 6.7; N, 4.65%. mp 68.1–71.9 °C (measured by DSC).

***N*-Cyclohexyl-3,4-dihydroisoquinolinium bis(trifluoromethanesulfonyl)imide [cHDHQM][NTf$_2$] 8c**. ^{1}H NMR (300 MHz, $CDCl_3$; TMS): δ_H/ppm = 1.25–2.18 (10H, m, J 13.2 Hz, J 3.6 Hz, $N{-}CH(C\underline{H_2}C\underline{H_2})_2C\underline{H_2}$), 3.24 (2H, t, J 7.8 Hz, $-C\underline{H_2}CH_2N$), 4.05 (3H, m, J 7.8 Hz, $-CH_2C\underline{H_2}N$, J 3.6 Hz, $N{-}C\underline{H}(CH_2CH_2)_2CH_2$), 7.27–7.83 (4H, m, $-C_6\underline{H_4}-$), 8.84 (1H, s, $-C\underline{H}{=}N$). ^{13}C NMR (75 MHz, $CDCl_3$; TMS): δ_C/ppm = 24.39, 24.53, 25.25; 30.63 ($N{-}CH(CH_2CH_2)_2CH_2$); 46.70, 70.70 ($-CH_2CH_2N-$); 117.28, 121.52 ($N(SO_2CF_3)_2$); 124.23, 128.16, 128.78, 134.38, 136.26, 138.54 ($-C_6H_4-$); 164.55 ($HC{=}N-$). MS EI (70 eV) *m*/*z*: 214 (100%) $[C_9H_9N{-}C_6H_{11}]^+$, 130 (74%) $[C_9H_8N]^+$. Elemental Analysis: Found: C, 40.6; H, 3.7; N, 5.3%; Calc. for $C_{17}H_{20}N_2O_4S_2F_6$: C, 41.3; H, 4.1; N, 5.7%. Density at 20 °C: 1.27 g cm^{-3}.

2.3. NMR spectra

NMR spectra were performed using Varian Unity Inova Plus spectrometer, 300 MHz for ^{1}H spectra and 75 MHz for ^{13}C spectra. All samples were dissolved in $CDCl_3$ 99.8% atoms of deuterium with 0.03 vol.% of TMS.

2.4. Differential scanning calorimetry (DSC)

DSC were performed using 822^e DSC Mettler Toledo Differential Scanning Analyzer. Sample of [RDHQM][X] (2–4 mg) was heated from 25 to 400 °C at a heating rate of 10 °C min^{-1} under nitrogen atmosphere.

2.5. Density measurement

Into pycnometer of known weight (m_{py} = 1.93 g) and known volume (V_{py} = 0.18 ml, determinated by water at 20 °C) was introduced an ionic liquid was thermostated in water bath at 20 °C for 15 min. After this time, pycnometer with the ionic liquid was dried and was weighed (m_s, ± 0.0001 g). For each ionic liquid procedure was repeated 4 times. Density of the ionic liquid (d_{IL}) was calculated according to equation:

$$d_{IL} = (m_s - m_{py})V_{py}^{-1}$$

2.6. General procedure for epoxidation

Sodium bicarbonate (5.0 equiv. mol), tetrabutylammonium hydrogen sulphate (0.1 equiv. mol), [RDHQM][X] (0.1 equiv. mol), olefin (0.10 g, 1.0 equiv. mol), water (6 ml) and acetonitrile (9 ml) were added to a three-necked flask fitted with a reflux condenser, a thermometer, a dropping funnel and a magnetic stirrer. A solution of Oxone® (2.0 equiv. mol) in water was added at room temperature. Oxone® is the trade name of salts mixture $2KHSO_5{\cdot}KHSO_4{\cdot}K_2SO_4$ in which $KHSO_5$ is an oxidising agent. After the addition was complete, the reaction mixture was kept at room temperature for 1 h and then heated to 60 °C. The reaction was maintained at this temperature for 20 h. The conversion of the starting materials was monitored by TLC using dichloromethane as the eluent and UV light and iodine in trichloromethane to visualise the signals. After this time, the reaction mixture was cooled to ambient temperature, and water was added to dissolve the inorganic solids. The contents of the flask were extracted with methylene chloride (4 × 15 ml). The organic layer was washed with 1% NaOH solution (5 × 15 ml) to remove [*n*-Bu$_4$N][HSO$_4$] and dried over anhydrous magnesium sulphate. The drying agent was removed by filtration, and the organic solvent was evaporated under high vacuum at 30–35 °C. The final product was analysed by ^{1}H and ^{13}C NMR spectroscopy.

1,2-Epoxycyclohexane 9b. ^{1}H NMR (300 MHz, $CDCl_3$; TMS): δ_H/ppm = 1.15–1.18 (2H, m, $-CH_2C\underline{H_2}C\underline{H_2}CH_2-$), 1.33–1.38 (2H, m, $-CH_2C\underline{H_2}C\underline{H_2}CH_2-$), 1.74–1.76 (2H, m, $-C\underline{H_2}CH_2CH_2C\underline{H_2}-$), 1.85–1.88 (2H, m, $-C\underline{H_2}CH_2CH_2C\underline{H_2}-$), 3.04–3.06 (2H, m, $\underline{H}C{-}O{-}C\underline{H}$). ^{13}C NMR (75 MHz, $CDCl_3$; TMS): δ_C/ppm = 19.45 ($-CH_2\underline{C}H_2\underline{C}H_2CH_2-$), 24.12 ($-\underline{C}H_2CH_2CH_2\underline{C}H_2-$), 52.01 ($H\underline{C}{-}O{-}\underline{C}H$).

1,2-Epoxycyclooctane 10b. ^{1}H NMR (300 MHz, $CDCl_3$; TMS): δ_H/ppm = 1.25–1.63 (8H, m, $-CH_2C\underline{H_2}C\underline{H_2}C\underline{H_2}C\underline{H_2}CH_2-$), 2.11–2.17 (4H, m, $-C\underline{H_2}CH_2CH_2CH_2CH_2C\underline{H_2}-$), 2.91 (2H, m,

Table 1
Results of the syntheses of 3,4-dihydroisoquinolinium *N*-substituted bromides.

Product	No.	Reaction time (h)	Yield[a] (%)	Melting point[b] (°C)	Density[c] (g cm^{-3})
[BDHQM][Br]	3a	6	84	–	1.40
[HDHQM][Br]	4a	16	73	–	1.32
[OcDHQM][Br]	5a	47	65	–	1.45
[DodDHQM[Br]	6a	24	71	52–54	–
[*i*-PDHQM][Br]	7a	20	91	–	1.63
[cHDHQM][Br]	8a	16	81	168–171	–

[a] Yield was determined for isolated products.
[b] Melting point of solids measured by capillary apparatus.
[c] Density of liquid products measured by pycnometer at 20 °C.

$\underline{H}C—O—C\underline{H}$). ^{13}C NMR (75 MHz, $CDCl_3$; TMS): δ_C/ppm = 25.48 (—$CH_2CH_2\underline{C}H_2\underline{C}H_2CH_2CH_2$—), 26.19 (—$CH_2\underline{C}H_2CH_2CH_2\underline{C}H_2CH_2$—), 26.44 (—$\underline{C}H_2CH_2CH_2CH_2CH_2\underline{C}H_2$—), 55.50 (H$\underline{C}$—O—$\underline{C}$H).

3. Results and discussion

3.1. Synthesis of N-substituted 3,4-dihydroisoquinolinium ionic liquids

A number of ionic liquids were obtained that contained the iminium group C=N—R. These substances are built from 3,4-dihydroisoquinolinium *N*-substituted cations that possess different substituents on the nitrogen atom.

They were obtained from isochroman (1) through a multi-step process (Fig. 3) [12,13]. An essential starting material for the synthesis of these derivatives is 2-(2-bromoethyl)benzaldehyde (2) [9], which was obtained as the product of the bromination of isochroman (1) [13]. Crude 2-(2-bromoethyl)benzaldehyde was reacted with primary amines to yield the desired 3,4-dihydroisoquinolinium *N*-substituted bromides (3a–8a). Fig. 4 shows the structures of the [RDHQM][Br] compounds that were synthesised and the abbreviations used in the remainder of this paper.

Table 1 shows the results of the synthesis of the 3,4-dihydroisoquinolinium *N*-substituted bromides (3a–8a). The reaction time for the condensation of the aldehyde with the primary amine depends largely on the type of the amine utilised; the duration of the reaction also considerably influences the final yield of the product.

The greatest yields were obtained for [i-PDHQM][Br] (91%), [BDHQM][Br] (84%) and [cHDHQM][Br] (81%). When using larger amines, longer reaction times were required to obtain high yields. At ambient temperature, some of the bromides were obtained as liquids with relatively high densitiy, in the range between 1.32 and 1.63 g cm^{-3}. An exception is [cHDHQM][Br] (8a), which is a solid having a melting point of 168–171 °C. The remaining 3,4-dihydroisoquinolinium *N*-substituted bromides that were obtained meet the defining criterion of ionic liquids [11].

Table 3
Effect of the type of atom on the chemical shift, δH, (300 MHz, $CDCl_3$; TMS) of the hydrogen atom of the —CH=N— group.

Cation	Anion		
	[Br]$^-$	[BF_4]$^-$	[NTf_2]$^-$
[BDHQM]$^+$	10.27 ppm	9.76 ppm	8.86 ppm
[HDHQM]$^+$	10.32 ppm	9.57 ppm	8.83 ppm
[OcDHQM]$^+$	10.38 ppm	9.70 ppm	8.80 ppm
[DodDHQM]$^+$	10.28 ppm	9.57 ppm	8.79 ppm
[*i*-PDHQM]$^+$	10.36 ppm	9.70 ppm	8.89 ppm
[cHDHQM]$^+$	10.30 ppm	9.71 ppm	8.84 ppm

The anion for each of the synthesised bromides was exchanged for tetrafluoroborate [BF_4]$^-$ and bis(trifluoromethylsulfonyl)imide [NTf_2]$^-$. These anions are commonly used in ionic liquids. The reactions were conducted as shown in Fig. 5.

Table 2 shows the results of these syntheses. As in the case of the bromides, most of the products containing the [BF_4]$^-$ and [NTf_2]$^-$ anions were liquids with relatively high density at room temperature, in the range between 1.27 and 1.69 g cm^{-3}. Under these conditions, [DodDHQM][BF_4] and [cHDHQM][BF_4] were solids with melting points lower than 100 °C. Therefore all of the compounds met the defining criterion of ionic liquids [11].

3.2. NMR data of N-substituted 3,4-dihydroisoquinolinium ionic liquids

The [RDHQM][X] structure was characterised using ^{1}H and ^{13}C NMR. The identity of the anion in the ionic liquid considerably influences the chemical shifts of the hydrogen atoms that are connected to the carbon atom of the iminium group [14,15]. The ^{1}H NMR data for these atoms are presented in Table 3.

Table 2
Results of the reaction in which [Br]$^-$ was exchanged for [BF_4]$^-$ or [NTf_2]$^-$.

Product	No.	Reaction time (min)	Yield[a] (%)	Melting point[b] (°C)	Density[c] (g cm^{-3})
[BDHQM][BF_4]	3b	10	69	37–40	–
[BDHQM][NTf_2]	3c	30	60	–	1.59
[HDHQM][BF_4]	4b	30	45	–	1.48
[HDHQM][NTf_2]	4c	60	50	–	1.69
[OcDHQM][BF_4]	5b	60	57	–	1.38
[OcDHQM][NTf_2]	5c	60	81	–	1.51
[DodDHQM][BF_4]	6b	10	72	56–58	–
[DodDHQM][NTf_2]	6c	30	38	–	1.60
[*i*-PDHQM][BF_4]	7b	60	79	–	1.43
[*i*-PDHQM][NTf_2]	7c	60	87	–	1.62
[cHDHQM][BF_4]	8b	60	63	74–77	–
[cHDHQM][NTf_2]	8c	60	50	–	1.27

[a] Yield was determined for isolated products.
[b] Melting point of solids measured by capillary apparatus.
[c] Density of liquid products measured by pycnometer at 20 °C.

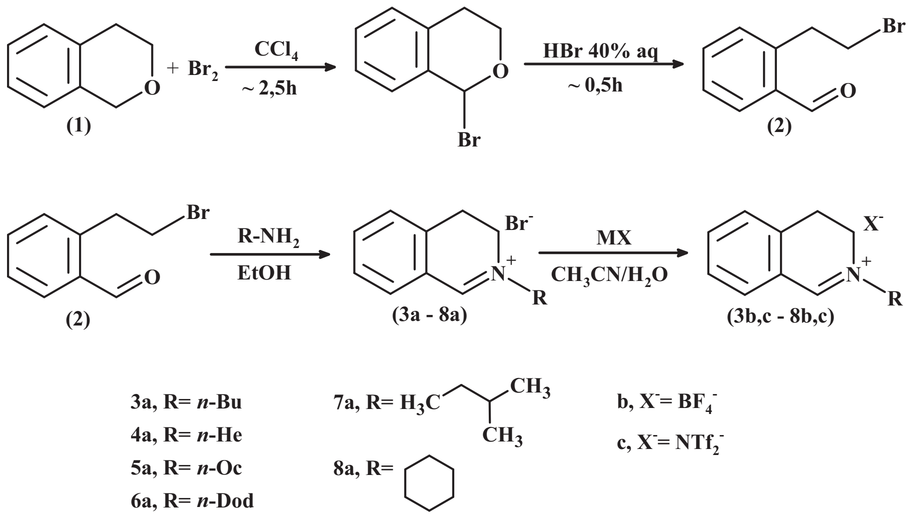

Fig. 3. Synthesis of [RDHQM][X] from isochroman.

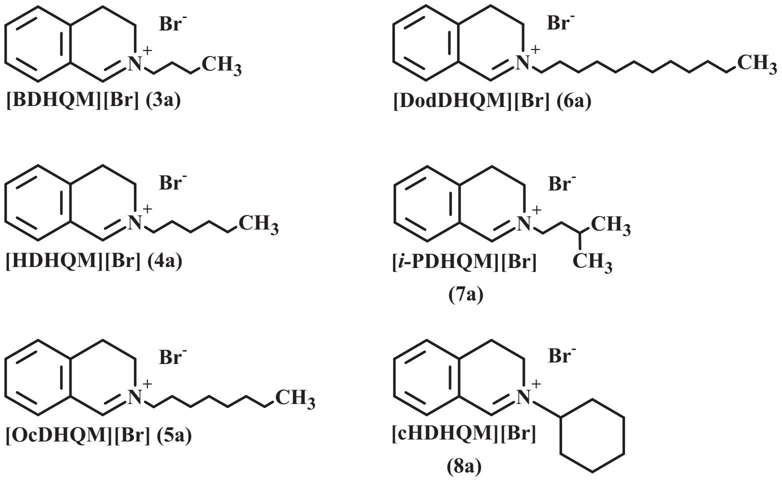

Fig. 4. Structures of the obtained [RDHQM][Br] compounds with their abbreviations.

The chemical shifts relative to TMS of the hydrogen atoms of the —CH=N— group for compounds containing the same anion were very similar (~10.32 ppm for $[Br]^-$, ~9.67 ppm for $[BF_4]^-$ and ~8.84 for $[NTf_2]^-$), regardless of the cation structure. In the series of synthesised compounds, the chemical shifts of this hydrogen atom were not affected by the characteristics of the substituent (length and shape of the hydrocarbon chain) on the nitrogen.

In contrast, the influence of the anion on the chemical shift of this hydrogen was clear. Amongst compounds containing the same cation, the variation in the chemical shift values due to specific anions ($\delta_H([Br]^-)$–$\delta_H([BF_4]^-) \approx 0.65$ ppm; $\delta_H([BF_4]^-)$–$\delta_H([NTf_2]^-) \approx 0.83$ ppm; $\delta_H([Br]^-)$–$\delta_H([NTf_2]^-)$ ≈ 1.48 ppm) was so large that the compounds can be easily differentiated based on the ^{1}H NMR spectra. This effect is caused by the differences in the cation-anion interactions and the formation of hydrogen bonds between these ions, as in the case of imidazolium ionic liquids [16]. When a proton is part of a hydrogen bond, a reduction in the shielding effect and a shift of the signal towards a higher value are observed. Amongst the anions utilised, the bromide ion interacts most strongly with the cation,

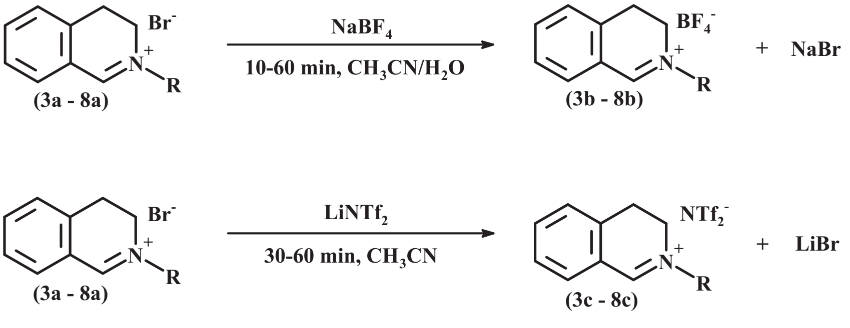

Fig. 5. Synthesis of $[RDHQM][BF_4]$ and $[RDHQM][NTf_2]$ from [RDHQM][Br].

Table 4
Chemical shift δ_C (75 MHz, $CDCl_3$; TMS) of the carbon atom of the $-\underline{C}H{=}N-$ group.

Cation	Anion		
	$[Br]^-$	$[BF_4]^-$	$[NTf_2]^-$
$[BDHQM]^+$	166.09 ppm	166.35 ppm	167.17 ppm
$[HDHQM]^+$	166.70 ppm	166.45 ppm	166.09 ppm
$[OcDHQM]^+$	166.50 ppm	166.92 ppm	166.05 ppm
$[DodDHQM]^+$	166.63 ppm	166.48 ppm	166.08 ppm
$[i\text{-PDHQM}]^+$	170.11 ppm	166.04 ppm	166.08 ppm
$[cHDHQM]^+$	165.35 ppm	165.16 ppm	164.55 ppm

whereas the other two anions have weaker interactions [17]. These interactions explain the differences in the chemical shifts of the proton of the iminium group; that is, this chemical shift depends on the type of the anion in the ionic liquid. The second reason for the differences in the chemical shifts of the hydrogen atom of the $-CH{=}N-$ group may be the structure of the anion. Anions that possess a larger number of atoms ($[NTf_2]^-$, $[BF_4]^-$) exert stronger shielding effects on this atom, and thus, the signal appears at a lower chemical shift. The signals of the remaining hydrogen atoms in the various cations were almost identical.

For the carbon atom of the iminium group (Table 4), a clear effect of the identity of the anion on the chemical shift was not observed. This carbon atom is linked with the more electronegative nitrogen atom by a double bond and has a higher chemical shift of approximately 166–167 ppm. For [cHDHQM][X] ionic liquids, we observed a slight shift in the signal of this carbon atom towards the stronger field. This observation may be explained by the cyclic structure of the substituent on the nitrogen atom.

3.3. *Thermal properties of N-substituted 3,4-dihydroisoquinolinium ionic liquids*

The thermal properties for synthesised [RDHQM][X] ionic liquids were investigated. The temperatures associated with phase transitions were measured by Differential Scanning Calorimetry (DSC), in the range 25–400 °C. The results of the analysis are shown in Table 5.

It is well known from the literature, that high thermal stability is the characteristic properity for ionic liquids [18,19]. As resulted from Table 5, all investigated [RDHQM][X] ionic liquids were stable to temperature of approximately 200 °C. The most stable ionic liquids were those with $[NTf_2]$ anions, and they underwent decomposition in temperature above 300 °C. It is typically characteristic for ionic liquids [20].

Table 5
Results of thermal analysis of sythesised [RDHQM][X].

Product	No.	Melting point (°C)[a]	T_{onset} (°C)[b]	T_{endset} (°C)[b]
[BDHQM][Br]	3a	–	223.1	294.5
$[BDHQM][BF_4]$	3b	43.2–47.3	236.4	299.6
$[BDHQM][NTf_2]$	3c	–	328.9	398.7
[HDHQM][Br]	4a	–	216.6	299.4
$[HDHQM][BF_4]$	4b	–	244.3	354.4
$[HDHQM][NTf_2]$	4c	–	302.8	435.0[c]
[OcDHQM][Br]	5a	–	229.4	310.6
$[OcDHQM][BF_4]$	5b	–	238.3	305.0
$[OcDHQM][NTf_2]$	5c	–	323.2	413.4[c]
[DodDHQM][Br]	6a	64.0–67.4	228.7	286.5
$[DodDHQM][BF_4]$	6b	58.0–60.3	223.5	325.5
$[DodDHQM][NTf_2]$	6c	–	311.6	397.4
[*i*-PDHQM][Br]	7a	–	312.6	376.2
$[i\text{-PDHQM}][BF_4]$	7b	–	239.9	291.7
$[i\text{-PDHQM}][NTf_2]$	7c	–	302.0	405.2[c]
[cHDHQM][Br]	8a	162.9–168.2	217.8	281.5
$[cHDHQM][BF_4]$	8b	68.1–71.9	263.0	307.1
$[cHDHQM][NTf_2]$	8c	–	319.6	384.7

[a] Melting point measured by DSC.
[b] The decomposition temperature determined by DSC.
[c] The decomposition temperature determined by TGA.

Table 6
Results of cyclohexene and cyclooctene epoxidation using [RDHQM][X] ionic liquids as catalysts.

Catalyst [RDHQM][X]	Catalyst No.	Product yield/%	
		1,2-Epoxycyclohexane (9b)	1,2-Epoxycyclooctane (10b)
$[BDHQM][BF_4]$	3b	46	44
$[BDHQM][NTf_2]$	3c	42	39
[HDHQM][Br]	4a	63	44
$[HDHQM][BF_4]$	4b	50	44
$[HDHQM][NTf_2]$	4c	73	58
[OcDHQM][Br]	5a	63	39
$[OcDHQM][BF_4]$	5b	54	35
$[OcDHQM][NTf_2]$	5c	67	51
[DodDHQM][Br]	6a	46	39
$[DodDHQM][BF_4]$	6b	46	31
$[DodDHQM][NTf_2]$	6c	59	47
$[cHDHQM][BF_4]$	8b	63	28
$[cHDHQM][NTf_2]$	8c	59	35

Conditions: 0.1 equiv. mol calatyst, 2.0 equiv. mol Oxone®, 5.0 equiv. mol Na_2CO_3, 0.1 equiv. mol $[n\text{-}Bu_4N][HSO_4]$, solvent acetonitrile/water = 1.5/1.0, temperature 60 °C, reaction time 20 h. Yield was determined for isolated products.

3.4. *Application of the synthesised ionic liquids as catalysts in olefin epoxidation*

An essential element of this study was the investigation of the potential use of the synthesised [RDHQM][X] ionic liquids as catalysts for epoxidation. Earlier, Philip C. Bulman Page et al. described application of the tetraphenylborate 3,4-dihydroisoquinolinium *N*-substituted salts as the efficient catalysts in olefins epoxidation reactions [21].

For our experiments, model alkenes such as cyclohexene (9a) and cyclooctene (10a) were selected. The epoxidation products of these alkenes have practical applications. 1,2-Epoxycyclohexane (cyclohexene oxide, CHO, 9b) is widely used in the chemistry and technology of polymers. The copolymerisation of CHO with carbon dioxide provides to biodegradable poly(cyclohexene carbonate)s [22]. In addition, CHO is used to modify polymeric resins that contain amino groups [23] and is used in the synthesis of pesticides, pharmaceuticals and dyestuff [24]. 1,2-Epoxycyclooctane (cyclooctene oxide, COO, 10b) has applications in the chemistry of organosilicon compounds [25,26]. Both of these epoxides may be easily converted into the corresponding vicinal diols, which are important intermediates in organic synthesis [27] and in polymer chemistry [28].

The epoxidation reactions were performed in the presence of [RDHQM][X] as a catalyst at a concentration of 10 mol% relative to the alkene. Potassium peroxymonosulphate ($KHSO_5$) was used as the oxidising agent (Fig. 6). The solvent for these reactions was a mixture of acetonitrile and water in a 1.5/1.0 ratio by volume. In addition, tetrabutylammonium hydrogen sulphate, $[n\text{-}Bu_4N][HSO_4]$, was utilised.

Table 6 shows the results of these reactions. The reactions were monitored by TLC. After 20 h, the starting materials were not observed in the reaction mixtures. The separated products of the reactions were characterised by ^1H and ^{13}C NMR spectroscopy.

The major products of these reactions were the epoxides: 1,2-epoxycyclohexane and 1,2-epoxycyclooctane. The reaction yields were determined for the isolated products and varied from 30 to 70%. In some cases of cyclohexene epoxidation, a trace amount of 1,2-cyclohexanediol was observed, as indicated by the

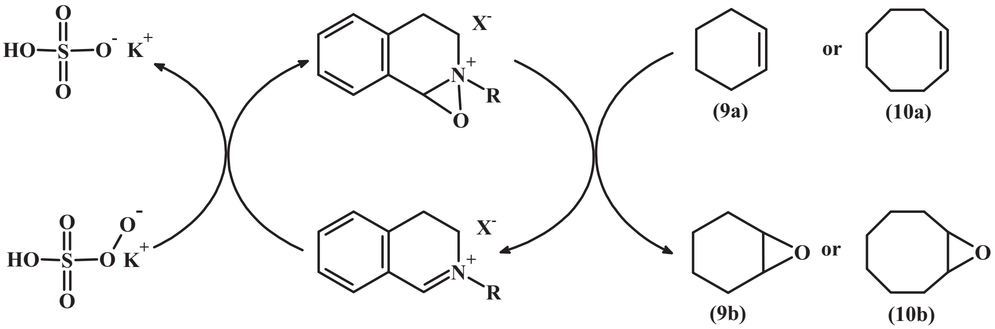

Fig. 6. Epoxidation of cyclohexene and cyclooctene using [RDHQM][X] ionic liquids as catalysts.

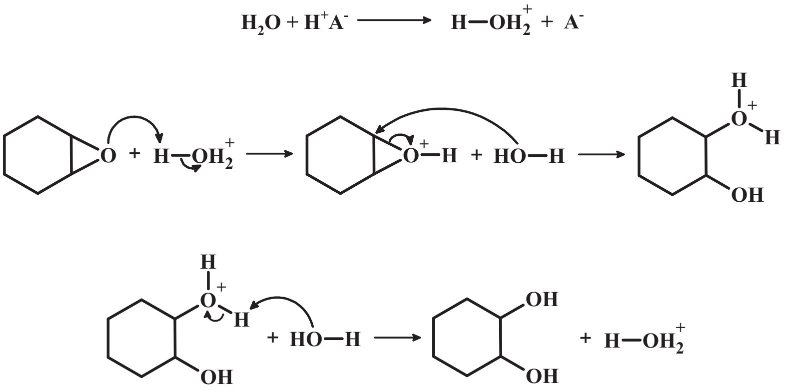

Fig. 7. Mechanism of 1,2-cyclohexanediol formation under aqueous acidic conditions.

corresponding weak signals in the NMR spectra (^{1}H NMR 300 MHz, $CDCl_3$, TMS: δ_H/ppm = 4.14, 2H, s, —O$\underline{H}$; ^{13}C NMR 75 MHz, $CDCl_3$, TMS: δ_C/ppm = 77.15, $\underline{C}$—OH). The presence of water and acidic substances in the reaction system promotes epoxide ring-opening and diol formation [29], as shown in Fig. 7.

When comparing the results of the epoxidation reactions of model alkenes using the same catalyst, the yield for the epoxidation of cyclohexene was higher than that for cyclooctene in all of the experiments; this result conflicts with the literature data [30]. In the cyclooctene epoxidation, secondary epoxide ring-opening by-products were not observed. In the absence of the undesirable side reactions, the lower yield of 1,2-epoxycyclooctane may be caused by the more difficult extraction and purification of this epoxide.

When comparing series of ionic liquids with the same cation, the best results were observed for compounds containing the hydrophobic bis(trifluoromethylsulfonyl)imide anion $[NTf_2]^-$ instead of $[BF_4]^-$ or $[Br]^-$ in most cases. For the $[BDHQM]^+$ (3b, 3c) and $[cHDHQM]^+$ (8b, 8c) series of ionic liquids, the yields of products were comparable for both anions, and a clear effect of the type of anion was not observed.

Our results show that the synthesised *N*-substituted 3,4-dihydroisoquinolinium ionic liquids may have uses as catalysts in olefin epoxidation.

4. Conclusions

Ionic liquids that contain an iminium group were synthesised based on an *N*-substituted 3,4-dihydroisoquinolinium cation and anions that are typically used in this type of compound, $[Br]^-$, $[BF_4]^-$ and $[NTf_2]^-$. The synthesis consisted of several steps. The duration of the reaction between 2-(2-bromoethyl)benzaldehyde and the primary amine was critical and strongly influenced the final yield of the product. A longer reaction time should be utilised for bulkier amines.

At ambient temperature, most products were high-density liquids, and only compounds with a relatively large cation and a small anion were solids. This relationship is characteristic of all types of ionic liquids.

The ^{1}H NMR and ^{13}C NMR spectra of the obtained isoquinolinium ionic liquids were determined. The type of anion influenced the chemical shift of the hydrogen on the carbon of the iminium group. For specific types of anions, this signal fell within a very narrow and characteristic range, and substances built from the same cation and different anions can be easily identified.

All of obtained [RDHQM][X] ionic liquids are stable to temperature of approximately 200 °C. The most stable are compounds with $[NTf_2]$ anion. $[RDHQM][NTf_2]$ decomposes in temperature above 300 °C. Slightly different of melting point value, measured by DSC and capillary apparatus was observed.

The synthesised [RDHQM][X] ionic liquids were tested as catalysts for the epoxidation of cyclohexene and cyclooctene at a concentration of 10 mol% relative to the alkene. The yield varied from 30 to 70%, but was higher for cyclohexene in all of the experiments. The starting materials were not detected in the reaction mixture after 20 h. The identity of each product was determined based on the ^{1}H NMR and ^{13}C NMR spectra. The reactions selectively produced the corresponding epoxides. In some of the cyclohexene epoxidation reactions, secondary epoxide ring-opening and hydrolysis to form 1,2-epoxycyclohexanediol was observed, but the extent of this side reaction was very small. Undesirable side reactions were not observed in the epoxidation of cyclooctene. For both of the epoxidated alkenes, the best results were observed when using ionic liquids that contained the $[NTf_2]^-$ anion.

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