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Vicinal functionalization of olefins: a facile route to direct synthesis of β-chlorohydrins and β-chloroethers

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An efficient and environmentally benign protocol for the synthesis of vicinal chlorohydroxy and chloromethoxy derivatives in a highly regioselective manner from olefins using NH_4Cl as a chlorine source and oxone as an oxidant in aqueous acetone and methanol is demonstrated. This methodology offers an additive and metal chloride free approach and is endowed with simple reaction conditions, high yields, broad substrate scope, and good functional group tolerance. Moreover, the aromatic substrates with terminal double bond exhibited merely Markovnikov selectivity, while the internal alkenes shown the exclusive regiocontrol and low to moderate diastereoselectivity.

Introduction

Halogen-containing organic compounds have received considerable attention from synthetic chemists as targets of synthesis, because they can be allowed to a variety of functional groups containing carbon, nitrogen, oxygen, and sulphur.[1] Over 2000 naturally occurring organochlorine compounds have been discovered,[2] and many of these compounds exhibit interesting biological activity of various kinds.[3] In many instances, the presence of chlorine atoms within the structures are responsible for either enhancing the biological activity or chemical stability and intrinsic potency of a natural product or a synthetic compound.[4] A few examples of naturally occurring bioactive polychlorides, such as chlorosulfolipids, have shown in figure 1.[5] In recent years, the increasing interest in chlorine-containing compounds spearheaded efforts to develop synthetic methodologies for stereoselective installation of sp^3C-Cl (sp^3 carbon-chlorine) bonds.[6]

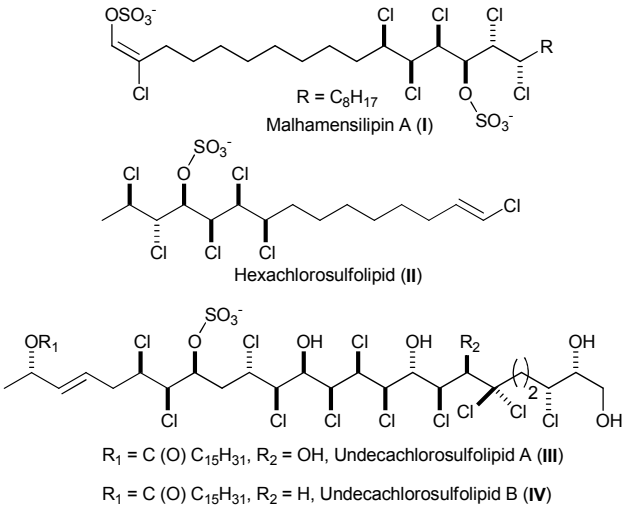

Fig. 1 Natural bioactive chlorosulfolipids (**I**-**IV**).

Chlorination constitutes one of the most important reactions in organic chemistry and has been widely studied in synthetic field.[7] Traditional chlorination processes uses molecular chlorine as chlorinating agent. To avoid difficulty with the use of hazardous, toxic, and corrosive gaseous chlorine, different chlorine surrogates under various conditions have been

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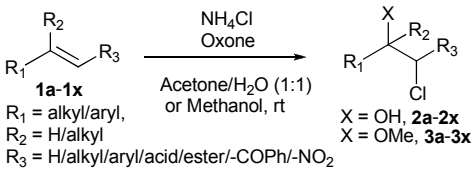
† Electronic Supplementaery Information (ESI) available: characterization data and copies of ^{1}H and ^{13}C NMR spectra for all the products. See DOI: 10.1039/b000000x/

utilized.[8] For instance, oxidative chlorination, via *in situ* generation of chlorinating agent from oxidation of chloride ion with a suitable oxidant, has emerged as a powerful tool for the production of chlorinated synthons.[9]

Vicinal functionalization of olefins, by selective introduction of two different functional groups in a highly regio- and stereo selective manner with the formation of two new bonds, is a powerful synthetic method which rapidly increases molecular complexity.[10] Vicinal halohydrin derivatives have found widespread applications in synthetic organic chemistry. Such halo derivatives serve as extremely versatile building blocks,[11] valuable bioactive materials,[12] and key intermediates.[13] One appealing approach for the synthesis of vicinal chlorohydrins involves the cleavage of epoxide ring with HCl or metal chlorides or other chlorine reagents.[11(a),14] Though these procedures have their own advantages, they also suffer from some limitations which include low atom efficiency with respect to direct conversion of alkenes to chlorohydroxy derivatives and require prior synthesis of epoxides from its precursors. Alternatively, a few reagent systems have been reported in the literature for direct transformation of carbon-carbon double bond to the corresponding 1,2-difunctionalized alkane i.e., chloroalcohol derivative. They include: chloramine T trihydrate or 1,3-dichloro-5,5-dimethylhydantoin (DCDMH) in N-tosyl-L-threonine (NTsLT)/*t*-BuOH/Water,[15] $NaIO_4$/NaCl or LiCl in 30% H_2SO_4/CH_3CN/H_2O,[16] trichlorocyanuric acid in acetone/H_2O,[17] and *N*-chlorosuccinimide (NCS)/thiourea in THF/H_2O.[18] However, most of the current methods usually have the disadvantages of using expensive reagents, acidic additives, metal chlorides or strong acids as chlorinating agents, catalyst, low yields, and limited applicability to olefinic substrates. Owing to the limitations of above-mentioned approaches and widespread interest in chlorine-containing compounds, still there is a need for development of a simple, efficient, and sustainable protocol for the production of chlorohydrins.

In a green chemistry point of view, avoiding toxic and/or hazardous reagents and solvents, diminishing energy consumption, more atom efficient, healthy, and safer reaction processes are highly desirable.[19] In our ongoing interest in the development of eco-friendly halogenation protocols,[9(c),20] earlier we have disclosed the oxidative chlorination of aromatic rings[20(a)] and carbonyl compounds.[20(b)] We report herein a facile synthesis of β-chlorohydrins and β-chloroethers from olefins using NH_4Cl as a chlorine source and oxone® as an oxidant under mild conditions in an environmentally preferred[21] solvents (Scheme 1).

Oxone® ($2KHSO_5.KHSO_4.K_2SO_4$), a potassium triple salt containing potassium peroxy monosulfate, is a commercially available, low-cost, non-toxic, and eco-friendly oxidant. Because of discovery of multiple innovative applications, oxone® is becoming an increasingly popular reagent for several organic transformations.[22(b)]

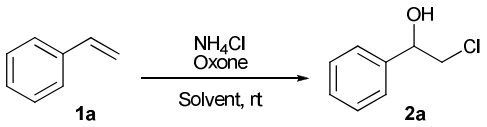


Scheme 1 Vicinal functionalization of olefins using NH_4Cl and oxone®.

Results and discussion

Initially, the reaction of styrene with NH_4Cl and oxone® was selected as a model reaction and the effect of solvent on reaction in terms of reaction time and yield was investigated (Table 1). A series of non-polar and polar solvents (single or their combination with water) were evaluated. The reaction in organic solvents or water alone not provided the desired chlorohydroxylation product **2a** in high yield (Table 1, entries 1-10). By changing the reaction medium to a mixture of non-polar solvent and water, the reaction time was decreased but low yield was observed. While, the water combination with polar solvents dramatically improved the yield of corresponding chlorohydrin (Table 1, entries 14-18). Remarkably, the best results were obtained when 1:1 mixture of acetone and water used as solvent system (Table 1, entry 15).

Table 1 1,2-Difunctionalization of styrene-effect of solvent[a,b]

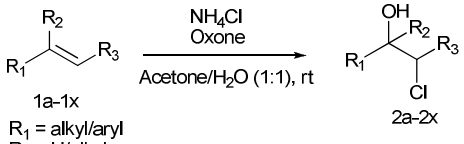


S. No.	Solvent	Time (h)	Yield (%)
1	DCM	24	00
2	$CHCl_3$	24	00
3	CCl_4	24	00
4	CH_3CN	24	<5
5	Acetone	24	<5
6	THF	24	<5
7	DME	24	<10
8	1,4-Dioxane	24	<10
9	Methanol	3.33	00
10	H_2O	1	21
11	DCM/H_2O (1:1)	0.66	<10
12	$CHCl_3$/H_2O (1:1)	0.66	<10
13	CCl_4/H_2O (1:1)	0.66	<10
14	CH_3CN/H_2O (1:1)	3.5	88
15	Acetone/H_2O (1:1)	3.5	95
16	THF/H_2O (1:1)	3.5	92
17	DME/H_2O (1:1)	3.5	73
18	1,4-Dioxane/H_2O (1:1)	3.5	79

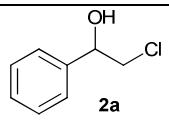
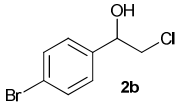
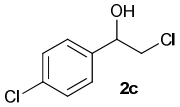
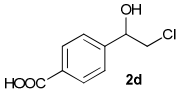
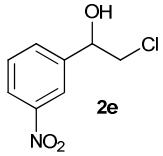
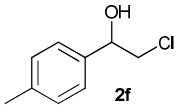
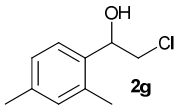
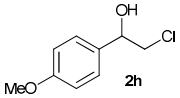
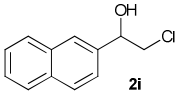
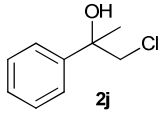
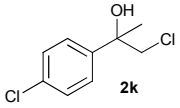
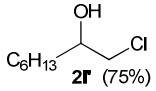
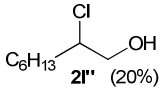
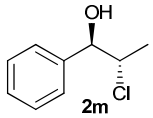
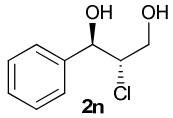
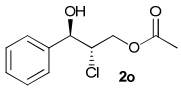
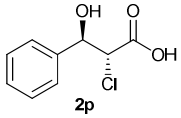
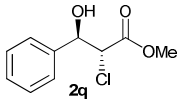
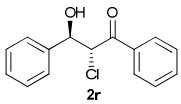
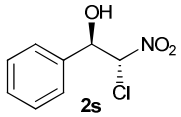
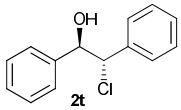
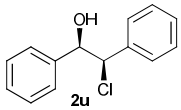
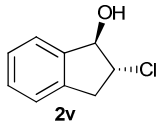
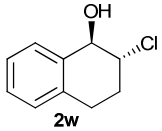
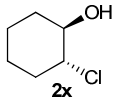
[a] Reaction conditions: substrate **1a** (2 mmol), NH_4Cl (2.2 mmol), oxone® (2.2 mmol), solvent (10 mL), room temperature. [b] The product was characterized by NMR spectroscopy and the yield was based on GC.

With the optimal conditions in hand, we proceeded to explore the utility and scope of the chlorohydroxylation with other alkenes. As is evident in Table 2, this method is compatible with a wide array of terminal (aromatic and

Table 2 Synthesis of β-chlorohydrins from olefins using NH_4Cl and oxone®[a,b,c]



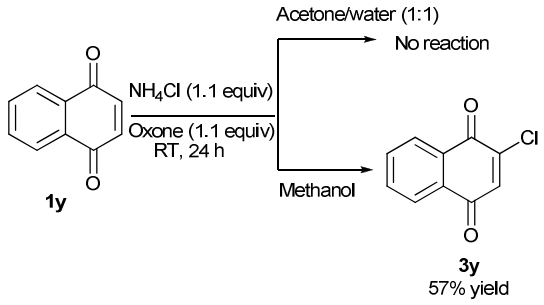
R_1 = alkyl/aryl
R_2 = H/alkyl
R_3 = H/alkyl/aryl/acid/ester/-COPh/-NO_2

Entry	Olefin	Time (h)	Product	Yield (%)	dr
1	**1a**	3.5	 **2a**	95	-
2	**1b**	4	 **2b**	90	-
3	**1c**	4	 **2c**	91	-
4	**1d**	4	 **2d**	81	-
5	**1e**	7	 **2e**	83	-
6	**1f**	3	 **2f**	83	-
7	**1g**	3	 **2g**	72	-
8	**1h**	1	 **2h**	82	-
9	**1i**	6	 **2i**	82	-
10	**1j**	1	 **2j**	91	-
11	**1k**	3.5	 **2k**	77	-
12	**1l**	0.5	 **2l'** (75%)	95	-
			 **2l''** (20%)		
13	**1m**	2.16	 **2m**	70	6.77:1
14	**1n**	1.25	 **2n**	88	5.28:1
15	**1o**	2	 **2o**	68	8:1
16	**1p**	24	 **2p**	22	10:1
17	**1q**	24	 **2q**	25	5.25:1
18	**1r**	24	 **2r**	NR[d]	-
19	**1s**	24	 **2s**	NR[d]	-
20	**1t**	6	 **2t**	63	1.42:1
21	**1u**	5	 **2u**	51	1.68:1
22	**1v**	3	 **2v**	81	3.34:1
23	**1w**	2	 **2w**	96	2.42:1
24	**1x**	0.33	 **2x**	98	11.25:1

[a] Reaction conditions: substrate (2 mmol), NH_4Cl (2.2 mmol), oxone® (2.2 mmol), acetone/H_2O (1:1; 10 mL), room temperature. [b] The products were characterized by NMR spectroscopy and yields were based on GC. [c] dr determined by crude ^1H NMR spectroscopy. [d] NR refers to no reaction was observed.

aliphatic) and 1,2-disubstituted (symmetrical and unsymmetrical) olefins. First, we tested the aromatic substrates

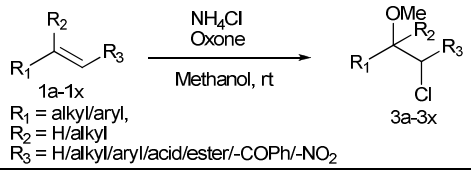
with terminal double bond and obtained the corresponding products **2a-2k** in good to excellent yields with exclusive Markovnikov regioselectivity (Table 2). The styrenyl substrates with deactivating groups on phenyl ring, such as 4-bromostyrene (**1b**), 4-chlorostyrene (**1c**), 4-vinylbenzoic acid (**1d**), and 3-nitrostyrene (**1e**) reacted smoothly to gave preferred chlorohydroxylation products **2b**, **2c**, **2d**, and **2e** in 90%, 91%, 81%, and 83% yields, respectively (Table 2, entries 2-5). While, those with activating substituents on phenyl group including 4-methylstyrene (**1f**), 2,4-dimethylstyrene (**1g**), and 4-methoxystyrene (**1h**), afforded the respective products **2f**, **2g**, and **2h** in 83%, 72%, and 82% yields, respectively (Table 2, entries 6-8). These results indicate that, the both activating and deactivating groups were well tolerated with the present reaction conditions. Polyaromatic olefin, i.e. 2-vinylnaphthalene (**1i**), also observed to be an excellent substrate for the reaction and generated the compound **2i** in 82% yield (Table 2, entry 9). In addition, the α-substituted styrene derivatives **1j** and **1k** were reacted in a similar manner and furnished the corresponding products **2j** and **2k** in 91% and 77% yields, respectively (Table 2, entries 10-11). Moreover, the aliphatic terminal alkene **1l** produced the corresponding vicinal chlorohydrins in 95% yield as a mixture of regioisomers **2l'** (75%) and **2l"** (20%) (Table 2, entry 12).



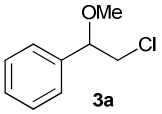
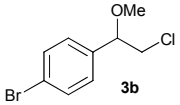
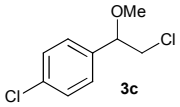
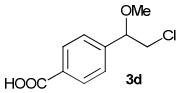
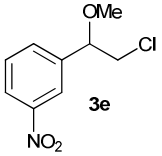
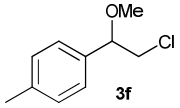
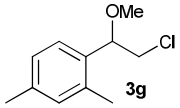
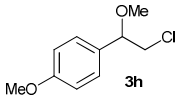
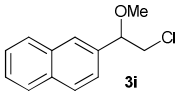
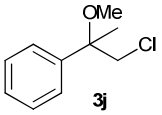
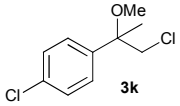
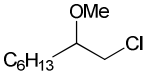
Scheme 2

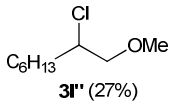
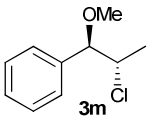
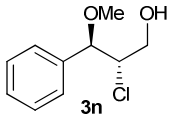
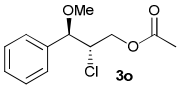
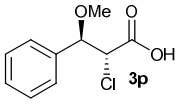
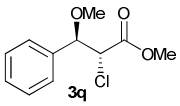
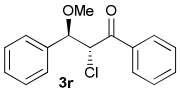
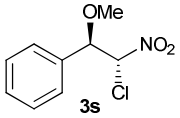
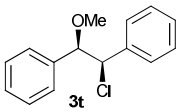
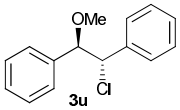
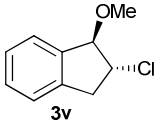
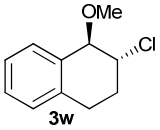
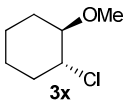
Sequentially, we examined the 1,2-disubstituted symmetrical and unsymmetrical olefins **1m-1x** under the same reaction conditions and obtained the corresponding products **2m-2x** with exceptional regiocontrol and low to moderate diastereoselectivity. The formation of the products **2m**, **2n**, and **2o** were observed in 70% (dr 6.77:1), 88% (dr 5.28:1), and 68% (8:1) yields, respectively, with exclusive α-hydroxy-β-chloro selectivity (Table 2, entries 13-15). Whilst, the deactivated olefin containing acid, ester, carbonyl, and/or nitro functionality with aryl substituent did not react completely even after 24 h and yielded the respective products with same regioselectivity albeit in low or zero yields (Table 2, entries 16-19). The both symmetrical disubstituted substrates, such as *cis*-stilbene (**1t**) and *trans*-stilbene (**1u**), generated the corresponding vicinal chlorohydroxy products **2t** and **2u** in 63% (dr 1.42:1) and 51% (1.68:1) yields, respectively (Table 2, entries 20-21), whereas in the case of 1,4-naphthoquinone (**1y**) reaction was not observed (Scheme 2). In addition, the aromatic cyclic alkenes **1v** and **1w** were used in this reaction to furnish merely Markovnikov

Table 3 Synthesis of β-chloroethers from olefins using NH_4Cl and oxone[®][a,b,c]



R_1 = alkyl/aryl,
R_2 = H/alkyl
R_3 = H/alkyl/aryl/acid/ester/-COPh/-NO_2

Entry	Olefin	Time (h)	Product	Yield (%)	dr
1	**1a**	3.33	 **3a**	90	-
2	**1b**	5	 **3b**	91	-
3	**1c**	3.5	 **3c**	91	-
4	**1d**	4	 **3d**	83	-
5	**1e**	9	 **3e**	88	-
6	**1f**	4	 **3f**	83	-
7	**1g**	6	 **3g**	64	-
8	**1h**	4	 **3h**	84	-
9	**1i**	10	 **3i**	90	-
10	**1j**	1.33	 **3j**	68	-
11	**1k**	6	 **3k**	83	-
12	**1l**	1.5	 **3l'** (55%)	82	-

			 **3l''** (27%)		
13	**1m**	6	 **3m**	79	5.58:1
14	**1n**	3	 **3n**	83	2.45:1
15	**1o**	2.25	 **3o**	61	9.16:1
16	**1p**	12	 **3p**	64	3.92:1
17	**1q**	5	 **3q**	90	4.62:1
18	**1r**	2.75	 **3r**	71	5.45:1
19	**1s**	24	 **3s**	50	5.25:1
20	**1t**	7	 **3t**	81	2:1
21	**1u**	4	 **3u**	86	1.38:1
22	**1v**	3	 **3v**	85	2.86:1
23	**1w**	3	 **3w**	92	2.28:1
24	**1x**	0.5	 **3x**	75	5:1

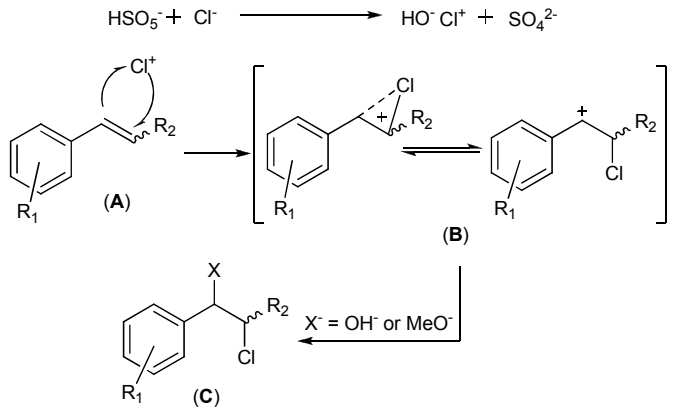
[a] Reaction conditions: substrate (2 mmol), NH_4Cl (2.2 mmol), oxone® (2.2 mmol), methanol (5 mL), room temperature. [b] The products were characterized by NMR spectroscopy and yields were based on GC. [c] dr determined by crude ^1H NMR spectroscopy.

products **2v** and **2w** in 81% (dr 3.34:1) and 96% (dr 2.42:1) yields, respectively (Table 2, entries 22-23). Moreover, the reaction of aliphatic cyclic olefin, i.e. cyclohexene (**1x**), resulted in the formation of the product **2x** in 98% yield with 11.25:1 diastereoselectivity in very short reaction time (Table 2, entry 24).

Inspired by the above results obtained for chlorohydroxylation of olefins in aqueous acetone under mild conditions, we then turned our attention to further investigate the same reaction in a nucleophillic alcoholic solvent, i.e. MeOH. In this context, a variety of olefins were subjected to the optimized conditions, used for chlorohydroxylation, in methanol and obtained the corresponding β-chloroether derivatives in good to excellent yields. The representative results of chloromethoxylation summarized in Table 3 indicate that, all the substrates **1a-1x** were compatible with these mild conditions. The reactions of styrenyl substrates and polyaromatic alkene (i.e. 2-vinylnaphthalene) were completely regiospecific and provided the corresponding α-methoxy-β-chloro derivatives **3a-3k** in yields ranging from 64 to 91%. Whereas, the reaction of terminal aliphatic olefin, i.e. 1-octene (**1l**), was non-regiospecific and afforded the mixture of regioisomers (**3l'** and **3l'')** (Table 3, entries 1-12). The use of 1,2-disubstituted symmetrical and unsymmetrical olefins generated the corresponding vicinal chloromethoxylation products **3m-3x** with highly regio- and low to moderate diastereoselectivities (Table 3). The activated olefinic substrates **1m**, **1n**, and **1o** furnished the corresponding vicinal functionalized products **3m**, **3n**, and **3o** in 79% (dr 5.58:1), 83% (dr 2.45:1), and 61% (dr 9.16:1) yields, respectively (Table 3, entries 13-15). Interestingly, the deactivated compounds **1p-1s** proceeded efficiently to gave the relevant products **3p-3s** in 50% to 90% yields (Table 3, entry 16-19). The treatment of the both *cis*- and *trans*-stilbenes yielded the respective products **3t** and **3u** in 81% (dr 2:1) and 86% (dr 1.38:1) yields, respectively (Table 3, entries 20-21). Surprisingly, the formation of product **3y** in 57% yield was observed when the symmetrical disubstituted substrate, i.e. 1,4-naphthoquinone (**1y**), used in this reaction (Scheme 2). Additionally, the aromatic and aliphatic cyclic olefins **1v-1x** under similar reaction conditions resulted in the formation of the desired products **3v**, **3w**, and **3x** in 85% (dr 2.86:1), 92% (dr 2.28:1), and 75% (dr 5:1) yields, respectively (Table 3, entries 22-24).

The above investigated results obtained for the both vicinal chlorohydroxylation and chloromethoxylation indicate that, all the aromatic olefins, irrespective of the substitution on double bond or phenyl ring, shown the exclusive Markovnikov regioselectivity based on the fact that the α-position (benzylic) is more positive than the β-position due to the presence of the aromatic ring. Moreover, most of the 1,2-disubstituted alkenes exhibited the predominant *anti*-stereoselectivity. The stereochemistry of the vicinal functionalized products is assigned based on ^1H NMR spectroscopy by comparing chemical shifts (δ) and coupling constants (J) of the protons attached to the carbon atoms bearing –Cl and –OH or –OMe with previously reported data.

A probable reaction pathway for the formation of β-chlorohydrins and β-chloroethers in a highly regioselective manner is illustrated in Scheme 3. It is assumed that, the Cl^- (NH_4Cl) ion is oxidized with oxone to generate Cl^+ (HOCl) ion *in situ*.[9(c),22] The electrophilic addition of Cl^+ ion onto the olefinic double bond (**A**) leads to the formation of a reactive intermediate (**B**). The intermediate (**B**) reacts with the nucleophile (OH^- or MeO^-) to afford the corresponding α-hydroxy or methoxy-β-chloro derivative (**C**).



Scheme 3 Probable reaction pathway for the formation of β-chlorohydrins and β-chloroethers.

Conclusions

In conclusion, we have developed a general and green approach, which utilizes environmentally friendly, cheap, and stable reagents (oxone and NH_4Cl), to vicinal functionalization of olefins. This methodology is applicable to a wide variety of olefinic substrates, which includes the terminal (aromatic and aliphatic) and 1,2-disubstituted (symmetrical and unsymmetrical) alkenes, and offers an economical and attractive avenue for the production of valuable synthetic intermediates bearing regio- and stereoselectively installed functionalities, including α-hydroxy-β-chloro and α-methoxy-β-chloro derivatives, under mild conditions at room temperature.

Experimental section

Typical procedure for vicinal functionalization of olefins

Oxone® (2.2 mmol) was slowly added to a well stirred solution of NH_4Cl (2.2 mmol) and olefin (2 mmol) in acetone-H_2O (1:1; 10 mL) or methanol (5 mL) and the reaction mixture was allowed to stir at room temperature, until olefin was completely disappeared (monitored by TLC, eluent: *n*-hexane-ethyl acetate). The organic layer was separated, and the aqueous phase was extracted with ethyl acetate (2x15 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography on silica gel (100-200 mesh) using *n*-hexane-ethyl acetate as eluent to give desired products.

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