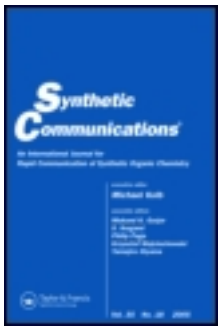

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Alkoxybromination of Olefins Using Ammonium Bromide and Oxone®

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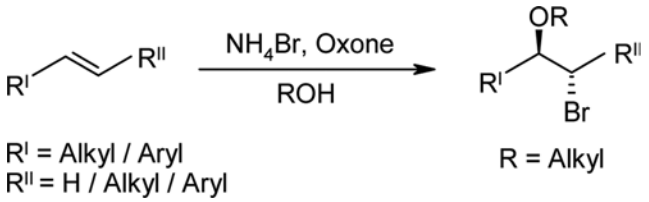
Abstract

A mild, efficient and highly regio- and stereoselective method for the methoxy and ethoxy bromination of olefins has been developed by using NH_4Br as a bromine source and Oxone® as an oxidant. Various kinds of olefins (aromatic, linear and cyclic olefins) afforded the corresponding alkoxy brominated products in moderate to excellent yields.

[Supplementary materials are available for this article. Go to the publisher's online edition of *Synthetic Communications*® for the following free supplemental resource(s): Full experimental and spectral details.]



KEYWORDS: alkenes; alkoxybromination; oxone®; regioselectivity; vicinal functionalization

INTRODUCTION

Halogenated organic molecules are found in many products, such as agrochemicals, pharmaceuticals, and molecules for advanced technologies. In organic synthesis, they are important intermediates in reactions involving metal cross-coupling reactions and organometallic preparations.[1]

The vicinal functionalization of olefins is an important process in synthetic organic chemistry, especially when the reaction is carried out in regio- and stereoselective fashion. Among the several methodologies found in the literature,[2] halofunctionalization[3] of alkenes towards synthetically useful substrates attract much more attention. For example, bromoalkoxylation of olefins is an important transformation in organic chemistry and the resulting alkoxybromides are important building blocks in organic, medicinal as well as industrial chemistry.[4]

Conventional bromination methods which typically use elemental bromine, is difficult to manipulate due to its toxicity, corrosiveness and high vapour pressure.[5] However, it is still being used by industry as well as academia due to its easy availability, low cost, and lack of a better alternative. In order to circumvent these problems, some alternative methods have been developed for the alkoxybromination of olefins such as isocyanuric acid,[6] (Ni,Al)-LDH-WO_4^{2-}-NH_4Br-H_2O_2,[7] $TSNBr_2$,[8] select fluor-KBr,[9] NBSP-KBr,[10] $NaIO_4$-LiBr,[11] $Yb(OTf)_3$-NBS,[12] NBS,[13] 2,4,4,6-tetrabromo-2,5-cyclohexadien-1-one,[14] *N,N'*-dibromo-2,5-piperazinedione,[15] $AgNO_3$-Ag_2O-Br_2,[16] methyl hypobromite,[17] $KBr/KBrO_3$.[18] However, most of these methodologies suffer from one or more disadvantages, such as use of expensive and hazardous/toxic reagents,

high reaction temperature, long reaction times, low yields, and tedious work-up procedures, which limit their use under the aspect of environmental benign process. Therefore replacement of such reagents by non-toxic, mild, selective, and easy-to-handle reagents is very desirable and represents an important goal in the context of clean synthesis.

Oxone® is a versatile oxidizing agent, which is easy to handle, water soluble, non-toxic, relatively inexpensive, and produces non-polluting byproducts. As a result, Oxone® has become an increasingly popular reagent for oxidative transformations.[19]

In continuation of our interest on the halogenation reactions using environmentally benign, easy to handle, and relatively inexpensive reagents,[20] recently we reported the hydroxy bromination and dibromination of olefins using NH_4Br/Oxone®.[21] Herein, we report, a simple method for the alkoxy bromination of olefins using NH_4Br/Oxone®. However, alkoxy bromination of olefins using NH_4Br/Oxone® has not been studied so far.

DISCUSSION

Initially methanolic solution of 1 equivalent of styrene was treated with 1.1 equivalents of NH_4Br and 1.1 equivalents of Oxone® at room temperature. After 50 minutes, complete disappearance of styrene was observed (indicated by TLC) and 2-bromo-1-methoxystyrene was formed in excellent yield (Table 1, entry 1). Here methanol served as the reaction medium as well as the nucleophile source. Encouraged by this result, we

decided to test the scope of other alcohols in the alkoxybromination of styrene at room temperature and 80°C and the data obtained were presented in Table 1. Among the different alcohols, primary alcohols (such as EtOH, *n*-PrOH and *n*-BuOH) gave the corresponding alkoxybromo products in good yields, while secondary (2-PrOH, 2-BuOH) and tertiary alcohols (*t*-BuOH) provided poor yields due to steric hindrance.

A number of different olefins were used as reactants in the methoxy and ethoxybromination with NH_4Br/Oxone® reagent system and results were summarized in Table 2 and 3. Activated, inactivated and moderately activated aromatic olefins furnished the respective 2-bromo-1-methoxy and 2-bromo-1-ethoxy products in high yields with-out forming any side-chain and ring brominated products (Table 2, entries 2-7).

Selectively *erythro* isomer was formed when asymmetric *trans*-alkenes were subjected to alkoxybromination (Table 2, entries 10-14). In ethanol a distinct difference of products were observed between room and reflux temperature with 4-phenyl-3-butene-2-one (**5**). At reflux temperature, the corresponding α-brominated product i.e. 1-bromo-4-phenyl-3-butene-2-one (**6**) was obtained in 50% yield. On the contrary, reaction at room temperature resulted in the formation of the respective double bond addition products i.e. ethoxybrominated (mixture of *erythro* and *threo* (65:35)) and dibrominated product (Scheme 1).

In case of symmetric olefins (Table 2, entries 15 and 16), *trans*-stilbene produced the corresponding *erythro*-methoxybromo product (**4o**), whereas *cis*-stilbene gave the

respective *threo*-methoxybromo product (**4p**) in methanol. In ethanol *trans*-stilbene yielded selectively *erythro*-ethoxybromo product (**4O**), whilst *cis*-stilbene furnished mixture of *threo* and *erythro* isomers.

Linear and cyclic olefins also provided good results with this reagent system (Table 3, entries 1-6). In case of linear olefins regioselectivity was not observed, for example 1-dodecene gave the corresponding Markovnikov's product (**4q**/**4Q**) and *anti*-Markovnikov product (**4q^{I}**/**4Q^{I}**), while mixed regioselectivity was observed for *trans*-2-octene (Table 3, entry 2). Exclusively Markovnikov's product was formed with 3-methyl-3-butene-1-ol and 1-methyl-1-cyclohexane (Table 3, entries 3 and 5). 1,4-naphthoquinone furnished the 2-bromo-1,4-naphthoquinone instead of the expected alkoxybrominated product in excellent yield (Table 3, entry 7). The stereochemistry of the products is confirmed by comparing the ^{1}H NMR coupling constant data of protons attached to the carbons bearing -OR and -Br groups of the alkoxybromides with previously reported data (see Supplymentary material).

EXPERIMENTAL

General

All chemicals used were reagent grade and used as received without further purification. ^{1}H NMR spectra were recorded at 300, 400 and 500 MHz and ^{13}C NMR spectra 75 MHz in $CDCl_3$ or DMSO-D_6. The chemical shifts (δ) are reported in ppm units relative to TMS as an internal standard for ^{1}H NMR and $CDCl_3$ for ^{13}C NMR spectra. Coupling constants (*J*) are reported in hertz (Hz) and multiplicities are indicated as follows: s (singlet), bs

(broad singlet), d (doublet), dd (doublet of doublet), t (triplet), m (multiplet). Mass spectra were recorded under impact (EI) conditions at 70 eV. Column chromatography was carried out using silica gel (finer than 200 mesh)

General Procedure For The Synthesis Of Alkoxybromides

To a solution of olefin (2 mmol) in MeOH/EtOH (10 ml) were added NH_4Br (2.2 mmol) and Oxone® (2.2 mmol) and the mixture was stirred at room/reflux temperature for the time shown in Table 2 and 3. After completion (as indicated by TLC), the reaction mixture was filtered and the solvent evaporated under reduced pressure. The products were purified by column chromatography over silica gel.

CONCLUSION

In summary, we have reported a general and efficient protocol for the regio- and stereoselective alkoxybromination of olefins using NH_4Br/Oxone® without catalyst. This method is applicable to different kinds of olefins, such as aromatic, linear, and cyclic olefins. The noteworthy feature of the present method is the use of NH_4Br/Oxone® system as a mild, non-toxic, inexpensive reagent system coupled with simple operation and formation of cleaner products with high yields. Another notable benefit of this system is that, in ethanol, 4-phenyl-3-butene-2-one gave the corresponding α-brominated product at room temperature and double bond addition products (ethoxybrominated and dibrominated product) at reflux temperature.

SUPPORTING INFORMATION

Full experimental detail, ^{1}H, ^{13}C NMR and mass spectra. This material can be found via the ‘‘Supplementary Content’’ section of this article’s webpage.’’

ACKNOWLEDGEMENTS

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iodination of carbonyl compounds using ammonium iodide and oxone. *Tetrahedron Lett.* **2011**, *52*, 6554-6559.

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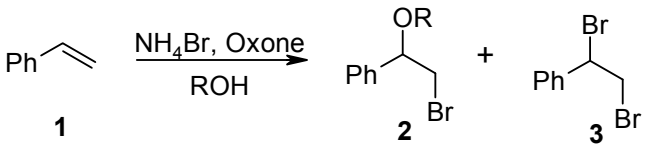
ACCEPTED MANUSCRIPT

Table 1. Alkoxybromination of styrene using various alcohols[a]



Entry	ROH	Time	Yield (%)[b]	
			2	**3**
1	MeOH	50 min[c]	85	<5
2	EtOH	24 h[c]	64	14
3	,,	2.45 h[d]	84	<5
4	*n*-PrOH	24 h[c]	55	22
5	,,	11 h[d]	70	9
6	*i*-PrOH	24 h[c]	30	41
7	,,	10 h[d]	35	12
8	*n*-BuOH	24 h[c]	50	15
9	,,	10 h[d]	61	<5
10	2-BuOH	24 h[c]	6	12
11	,,	12 h[d]	8	<5
12	*i*-BuOH	24 h[c]	25	19
13	,,	12.3 h[d]	34	10
14	*t*-BuOH	42 h[c]	7	30
15	,,	10.3 h[d]	22	55

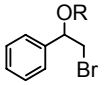
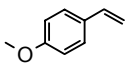
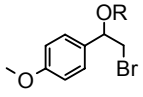
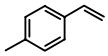
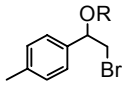
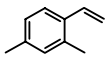
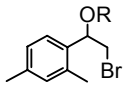
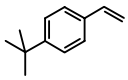
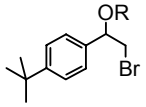
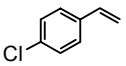
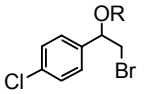
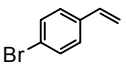
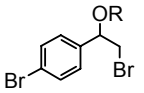
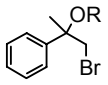
[a]Styrene (2 mmol), NH_4Br (2.2 mmol), Oxone® (2.2 mmol), ROH (10 mL).

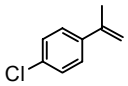
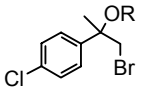
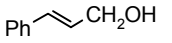
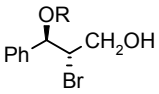
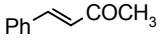
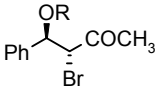
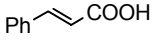
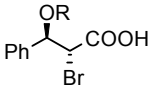
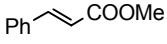
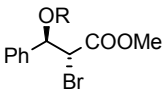
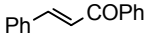
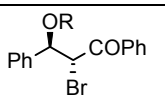
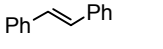
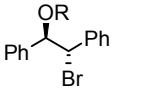
[b]Isolated yields.

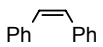
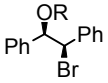
[c]At room temperature.

[d]At 80°C.

Table 2. Methoxy and Ethoxybromination of various aromatic olefins

Entry	Olefin	Product	R	Time	Yield (%)[a]
1			Me Et	50 min[b] 2.45 h[c]	85 (**4a**)/<5[e] 84 (**4A**)/<5[e]
2			Me Et	40 min[b] 2 h[c]	90 (**4b**) 92 (**4B**)
3			Me Et	15 min[b] 45 min[c]	93 (**4c**) 84 (**4C**)/<5[e]
4			Me Et	6 min[b] 1.15 h[c]	80 (**4d**)/<5[e] 75(**4D**)/<5[e]
5			Me Et	15 min[b] 2.30 h[c]	76 (**4e**)/<5[e] 80 (**4E**)
6			Me Et	30 min[b] 3 h[c]	91 (**4f**) 85 (**4F**)
7			Me Et	1 h[b] 3 h[c]	84 (**4g**)/<5[e] 85 (**4G**)
8			Me Et	13 min[b] 2.15 h[c]	92 (**4h**) 83 (**4H**)

9			Me Et	15 min[b] 2 h[c]	88 (**4i**) 72 (**4I**)/6[e]
10			Me Et	40 min[b] 3.30 h[c]	84[f] (**4j**)/<5[e] 89[f] (**4J**)
11			Me	2.15 h[b]	76[f] (**4k**)/5[e]
12			Me Et	2.30 h[b] 24 h[d]	76[f] (**4l**)/<5[e] 31[f] (**4L**)/29[e]
13			Me Et	3 h[b] 24 h[d]	71[f] (**4m**)/14[e] 20[f] (**4M**)/35[e]
14			Me Et	1 h[b] 3.3 h[c]	70[f] (**4n**)/10[e] 75[h] /<5[e]
15			Me Et	1.3 h[b] 3.3 h[c]	80[f] (**4o**)/<5[e] 76[f] (**4O**)/6[e]

16			Me Et	1 h[b] 1.3 h[c]	73[g] (**4p**)/5[e] 40[i] /10[e]

[a]Isolated yields.

[b]Olefin (2 mmol), NH_4Br (2.2 mmol), Oxone® (2.2 mmol), MeOH (10 mL) at room temperature.

[c]Olefin (2 mmol), NH_4Br (2.2 mmol), Oxone® (2.2 mmol), EtOH (10 mL) at reflux temperature.

[d]At room temperature.

[e]Dibromo product.

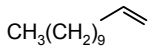
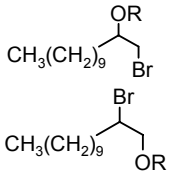
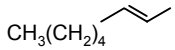
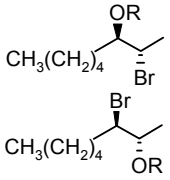
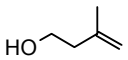
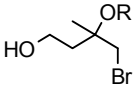
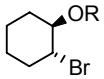
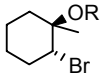
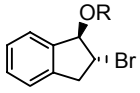
[f]e*rythro* products.

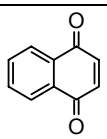
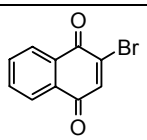
[g]*threo* products.

[h]Molar ratio of *erythro* and *threo* 62:38, determined by ^{1}H NMR.

[i]Molar ratio of *threo* and *erythro* 33:67, determined by ^{1}H NMR.

Table 3. Methoxy and Ethoxybromination of various linear and cyclic olefins

Entry	Olefin	Products	Time		Yield (%)[a]	
			R=Me	R=Et	R=Me	R=Et
1			45 min[b]	4 h[c]	60 (**4q**)/12[e] 5 (**4q^{I}**)	54 (**4Q**)/20[e] 5 (**4Q^{I}**)
2			45 min[b]	4 h[c]	24 (**4r**)/16[e] 39 (**4r^{I}**)	18 (**4R**)/21[e] 33 (**4R^{I}**)
3			30 min[b]	2.3 h[c]	75 (**4s**)/6[e]	63 (**4S**)/20[e]
4			5 min[b]	24 h[d]	64 (**4t**)/15[e]	34(**4T**)/32[e]
5			10 min[b]	24 h[d]	71 (**4u**)/10[e]	66(**4U**)/14[e]
6			15 min[b]	4 h[c]	76 (**4v**)/5[e]	81 (**4V**)/<5[e]

7			24 h[b]	5.3 h[c]	68 (**4w**)	73(**4w**)

[a]Isolated yields.

[b]Olefin (2 mmol), NH_4Br (2.2 mmol), Oxone® (2.2 mmol), MeOH (10 mL) at room temperature.

[c]Olefin (2 mmol), NH_4Br (2.2 mmol), Oxone® (2.2 mmol), EtOH (10 mL) at reflux temperature.

[d]At room temperature.

[e]Dibromo product.

Scheme 1. Bromination of 4-phenyl-3-butene-2-one in ethanol