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Regio- and Stereoselective Co-Iodination of Olefins using NH_4I and Oxone®

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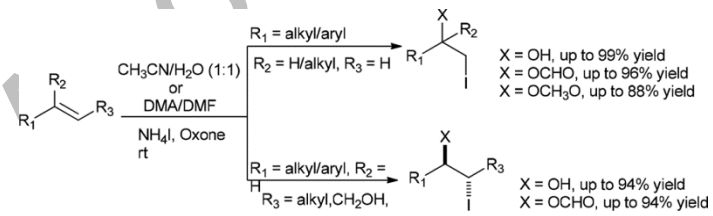
ABSTRACT

A simple, efficient and environmentally benign protocol for the synthesis of vicinal iodohydrins and iodoesters from olefins using NH_4I and oxone® in CH_3CN:H_2O (1:1) and DMF/DMA, respectively, without employing a catalyst at room temperature is described. Regio- and stereo selective iodohydroxylation and iodoesterification of various olefins with anti fashion, following Markonikov's rule was achieved and the corresponding products were obtained in good to excellent yields. In addition, 1,2-disubstituted olefins afforded excellent diastereoselectivity.

GRAPHICAL ABSTRACT



KEYWORDS: Co-Iodination; Diastereoselectivity; NH_4I; Olefins; Oxone®

INTRODUCTION

Vicinal functionalization of olefins is a remarkable fundamental process in organic synthesis, especially when the reaction affords products in regio- and stereoselective manner. In particular, simultaneous installation of two different functional groups, such as hydroxy or ester and halogen, have attracted much attention in synthetic organic chemistry.[1] Vicinal halohydrin derivatives have extensive applications in modern organic synthesis and they serve as highly adaptable building blocks,[2] valuable bioactive materials[3] and key intermediates.[4] Production of halohydrins from alkenes is a well-known procedure.[5] Iodohydrines cannot be prepared by the direct reaction of olefins with water solutions of the iodine, in contrast with their homologous chloro- and bromohydrins, because reversibility of the addition of hypoiodous acid to the double bond. Indeed, in most cases, an iodide ion scavenger[6] is generally needed to obtain satisfactory yields.

Some other protocols include the use of $H_5IO_6/NaHSO_3$,[7] *N*-iodoimides,[8] *N*-iodosaccharin,[9] bis(pyridine)iodine(I)salts,[10] DMDO/MeI,[11] triodide ion,[12] K10-MX/I_2/MWI,[13] IBX-I_2[14] and I_2/H_2O/clays[15] for the vicinal iodohydroxylation of alkenes have also been reported. Alternatively, iodohydrins are accessible from epoxides using different reagents, such as hydroiodicacid,[16] I_2/crown ethers,[17] Ti(O-i-Pr)$_4$/I_2 complex,[18] metal iodides[19] or ionic liquid.[20] Iodohydrins could also be synthesized from carbonyl compounds with CH_2I_2 (iodomethylation) in the presence of SmI_2[21] or halogen exchange reaction[22] of other halohydrins. However, most of the current methods usually have disadvantages of using expensive and toxic reagents, tedious work-up

procedures, producing low yields and limited applicability to olefinic substrates. Due to the limitations of the above mentioned approaches and the wide spread attention in iodine containing compounds, there is a need for the development of an efficient and sustainable method for the production of iodohydrins and iodoesters.

Oxone® ($2KHSO_5.KHSO_4.K_2SO_4$), a potassium triple salt containing potassium peroxymonosulfate, is a white crystalline solid, easy to handle, soluble in water and yields non-polluting byproducts. Because of the discovery of multiple innovative applications, oxone® has become an increasingly popular reagent for several organic transformations.[23] In continuation of our efforts toward the development of novel and eco-friendly halogenation protocols,[24],[25],[26] herein we report a facile method for the synthesis of β-iodohydrins and β-iodoesters from olefins using NH_4I as a iodine source and oxone® as an oxidant under mild conditions in CH_3CN:H_2O (1:1) and DMF/DMA, respectively, without employing a catalyst (Scheme 1).

RESULTS AND DISCUSSION

Initially, we investigated the iodohydroxylation of styrene with NH_4I and oxone® in various non-polar and polar solvents (single or their combination with water) and the results are described in Table 1. The results revealed that the water combination with polar solvents significantly improved the yield of corresponding iodohydrin (Table 1, entries 13-17). Remarkably, the best results were obtained when a mixture of CH_3CN and water was (1:1) used as a solvent system among others in terms of reaction yield and time (Table 1, entry 13).

With the optimal conditions in hand, the scope and limitations of the method were explored (Scheme 1) with a variety of alkenes (terminal and internal alkenes) and the results are presented in Table 2. First, we examined the aromatic substrates with a terminal double bond and obtained the corresponding products **1a–j** in good to excellent yields with exclusive Markovnikov regioselectivity (Table 2). Aromatic terminal alkenes with activated phenyl ring including 4-methoxystyrene (**1b**), 4-methylstyrene (**1c**) and 2,4-dimethylstyrene (**1d**) furnished the respective products **2b**, **2c** and **2d** in 72%, 95% and 91% yields, respectively (Table 2, entries 2-4). Whereas, in the case of 3-nitrostyrene (**1g**), longer reaction time (60 min) was required compared to activated aromatic alkenes to give the corresponding product (**2g**) in good yield (78%) (Table 2, entry 7). Halo substituted styrenes such as 4-chlorostyrene (**1e**) and 4-bromostyrene (**1f**) generated the corresponding iodohydroxylation products **2e** and **2f** in excellent yields due to the inductive and resonance effect of halogen (Cl, Br) groups (Table 2, entries 5 and 6). Unfortunately, 2-vinylpyridine (**1h**) failed to react even for prolonged reaction time (24 h) and recovered in quantitative yield (Table 2, entry 8). Polyaromatic alkene, *i.e.* 2-vinylnaphthalene (**1i**) also reacted well and afforded the respective product **2i** in 80% yield (Table 2, entry 9). In addition, the *α*-substituted styrene derivative (**1j)** provided the corresponding product (**2j)** in 97% yield (Table 2, entry 10) under similar conditions.

Subsequently, 1,2-disubstituted unsymmetrical and symmetrical olefins were submitted to the vicinal iodohydroxylation and produced the corresponding products **2k**-**2o** in good to excellent yields with excellent diastereoselectivity (Table 2). In all cases, complete

regio- and predominant *trans*-diastereoselective addition was observed. Unsymmetrical *trans*-alkenes **1k** and **1l** selectively formed the corresponding *erythro* isomers **2k** and **2l** in 84% and 75% yields, respectively (Table 2, entries 11 and 12). Symmetrical and unsymmetrical cyclic olefins, such as indene (**1m**), 1,2-dihydronaphthalene (**1n**) and cyclohexene (**1o**) reacted smoothly and yielded the corresponding products **2m**, **2n** and **2o** in 95%, 92% and 93% yields, respectively (Table 2, entries 13-15). In case of monosubstituted linear olefin, a limited *anti*-Markovnikov product was also observed. For example, 1-octene (**1p**) gave the corresponding Markovnikov's product (**2p**) (76%) as well as *anti*-Markovnikov's product (**2p^1**) (23%) (Table 2, entry 16). Mixed regioselectivity was observed with linear asymmetric *trans*-alkene, *i.e.*, *trans*-2-octene (**1q**) furnished the *erythro*-2-iodo-3-octanol (**2q**) and *erythro*-3-iodo-2-octanol (**2q^1**) in the ratio of 32:62 (Table 2, entry 17).

Interestingly, when DMF or DMA was used as a reaction medium under similar reaction conditions, the iodoester product was obtained instead of the expected iodohydrin (Table 1, entries 18 and 19). Stimulated by these affirmative preliminary results, subsequently, we considered to develop a methodology for the iodoesterification of alkenes. Only a few methods have been reported for the preparation of iodoesters directly from olefins such as KIO_3,[27] tetrafluoroboricacid/I_2/copper(II) oxide,[28] dichloroiodoisocyanuric acid/Ac_2O,[29] $Fe_2(SO_4)_3/I_2$,[30] $Ce(OTf)_4/I_2$[31] $NH_4I/H_2O_2/Ac_2O$.[32] To improve the yield of iodoformate (**3a**), styrene (1 mmol) was allowed to react with different mole ratios of oxone® (1.0, 1.1) in the presence of NH_4I (1.1) in DMF (10 mL) (Table 1, entries 20 and 21). The results revealed that a 1 : 1.1 :

1.1 mole ratio of styrene, oxone® and NH_4I at room temperature was the optimum reaction conditions for iodoformyloxylation of olefins.

Under the optimized conditions, we successfully carried out the iodoformyloxylation of various olefins by using DMF as a nucleophilic solvent and obtained the corresponding *β*-iodoformate derivatives in good to excellent yields (Table 3). Olefins having either activated (**1b-c**) or inactivated arenes (**1d-f**) reacted well and furnished the respective vicinal iodoformate products **3b-f** in 70-94% yields. Heteroaromatic olefin (**1g**) and 2-vinylnaphthalene (**1h**) also provided the corresponding products **3g** and **3h** in 90% and 82% yields, respectively (Table 3, entries 7 and 8). The use of 1,2-disubstituted symmetrical and unsymmetrical olefins generated the corresponding vicinal iodoformyloxylation products **3i**-**3k** with high regio- and excellent diastereoselectivities (Table 3). The activated olefinic substrates **1i** and **1j** selectively yielded the corresponding *erythro* isomer products **3i** and **3j** in 79% and 92% yields, respectively (Table 3, entries 9-10). Similarly, cyclic olefin (**1k**) afforded the respective vicinal iodoformate product **3k** in 94% yield (Table 3, entry 11). Linear aliphatic olefins (**1l** and **1m)** gave the corresponding Markovnikov's products (**3l** and **3m**) as well as *anti*-Markovnikov products (**3l**[1] and **3m**[1]) (Table 3, entries 12 and 13). However, *erythro* isomer products were exclusively obtained for *trans*-2-octene (**1m**) (Table 3, entry 13).

Inspired by the above results obtained for the iodoformyloxylation of olefins in DMF as a nucleophilic solvent under mild conditions, we then turned our attention to further investigate the iodoacetoxylation of olefins in an another nucleophilic solvent *i.e.* DMA.

Unfortunately, activated aromatic olefins provided the corresponding iodohydrin derivatives instead of iodoacetates (Table 4, entries 2-4), whereas inactivated aromatic olefins reacted well and furnished the respective iodoacetate products in good to excellent yields (Table 4, entries 5-8).

A probable mechanistic pathway for the formation of iodohydrins and iodoesters from olefins is depicted in Scheme 2. It is assumed that oxone® efficiently oxidizes the I^- (NH_4I) to I^+ (HO^-I^+), which further reacts (electrophilic addition) with olefin **I** to give a three membered cyclic iodonium ion intermediate **II**. The cyclic intermediate **II** undergoes ring opening by the oxygen of DMF or DMA via S_N2 pathway to produce an iminium ion **III** intermediate, which upon hydrolysis gave the vicinal iodoester product **IV**. In case of iodohydrin formation, intermediate **II** reacts with the nucleophile (OH^-) in same manner to afford the corresponding α-hydroxy *β*-iodo derivative (**V**).

In all aromatic olefins, for both the vicinal iodohydroxylation and iodoesterification, the incoming nucleophile attacks at the benzylic position of cyclic intermediate exclusively. The regioselectivity of aromatic olefins can be explained by considering the fact that the *α*-position (benzylic) is more positive than the *β*-position because of the presence of the aromatic ring. Nucleophilic ring opening of the cyclic iodonium intermediate presumably takes place from the more positive *α*-position. Furthermore, most of the 1,2-disubstituted alkenes exhibited predominant *anti* stereoselectivity. The stereochemistry of the products was confirmed by analysis of the ^1H NMR data.

CONCLUSIONS

In conclusion, we have demonstrated a novel and highly efficient approach for the regio- and stereoselective iodohydroxylation and iodoesterification of olefins using NH_4I-oxone® reagent system. This method is applicable to different kinds of olefins, such as terminal, 1,2-disubstituted unsymmetrical and symmetrical olefins. The present protocol offers several advantages including commercial availability of the reagents, high yields, mild reaction conditions, high atom economy (100% with respect to iodine), no evolution of hydrogen iodide, high regio- and stereo selectivity of the reactions, economical process with easier setup/work-up procedures and environmental friendly. Hence it offers useful alternative to the existing methods.

EXPERIMENTAL SECTION

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). Column chromatography was carried out using silica gel (100-200 mesh).

General Procedure For Vicinal Iodohydroxylation Of Olefins

Oxone® (0.461 g, 0.75 mmol) was slowly added to a well stirred solution of NH_4I (0.160 g, 1.1 mmol) and olefin (1 mmol) in CH_3CN:H_2O (1:1) (10 mL) and the reaction mixture was allowed to stir at room temperature for the time shown in Table 2. When the reaction completion (TLC) or an appropriate time, the mixture was filtered and the solvent was evaporated under reduced pressure. The residue was dissolved in EtOAc (25 mL) and the solution was filtered and washed successively with 0.2 M aq $Na_2S_2O_3$ and H_2O. The organic layer was dried (Na_2SO_4) and concentrated in vacuo. The crude product was purified by column chromatography (silica gel, 5–50% EtOAc-hexane) to give pure products. All the products were identified on the basis of ^{1}H NMR, ^{13}C NMR and Mass spectroscopy.

General Procedure For Vicinal Iodoesterification Of Olefins

An olefin was slowly added to a well stirred (30 min) solution of NH_4I (0.160 g, 1.1 mmol) and oxone® (0.676 g, 1.1 mmol) in DMF/DMA (10 mL) and the reaction mixture was stirred at room temperature until the olefin completely disappeared (monitored by TLC) or an appropriate time, quenched with ice water and extracted with Et_2O (2 x 15 mL). Than the combined organic layers were washed with 0.2 M aq $Na_2S_2O_3$ and H_2O, dried (Na_2SO_4) and concentrated in vacuo. The resulting crude residue was purified by column chromatography (silica gel, 5-50% EtOAc-hexane) to give pure products. All the products were identified on the basis of ^{1}H NMR, ^{13}C NMR and Mass spectroscopy.

SUPPLEMENTARY MATERIAL

Experimental details and ^{1}H and ^{13}C NMR spectral data for this article can be accessed on the publisher's website.

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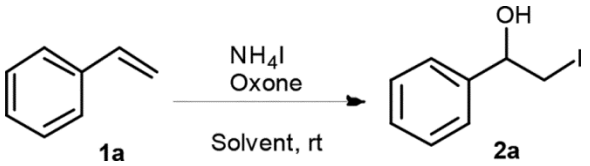
Table 1. Iodohydroxylation of styrene-effect of solvent[a]



S. No.	Solvent	Time (h)	Yield[b] (%)
1	DCM	24	8
2	$CHCl_3$	24	00
3	CCl_4	24	00
4	CH_3CN	24	78
5	Acetone	24	25
6	THF	24	28
7	DME	24	00
8	1,4-Dioxane	24	8
9	H_2O	24	80
10	DCM-H_2O (1:1)	0.1	15
11	$CHCl_3$-H_2O(1:1)	0.1	10
12	CCl_4-H_2O (1:1)	0.1	20
13	CH_3CN-H_2O (1:1)	0.1	99
14	AcetoneH_2O(1:1)	0.1	60
15	THF/H_2O (1:1)	0.1	78
16	DME/H_2O (1:1)	0.1	30
17	1,4-Dioxane/H_2O (1:1)	0.1	40
18	DMF	4	00 (48)[c]

19	DMA	4	00 (45) [d]
20	DMF	4	00 (85)[e]
21	DMF	4	00 (96)[f]

[a] Reaction conditions: substrate **1a** (1 mmol), NH_4I (0.160 g, 1.1 mmol,), oxone® (0.461 g, 0.75 mmol,), solvent (10 mL), room temperature.

[b] Isolated yields.

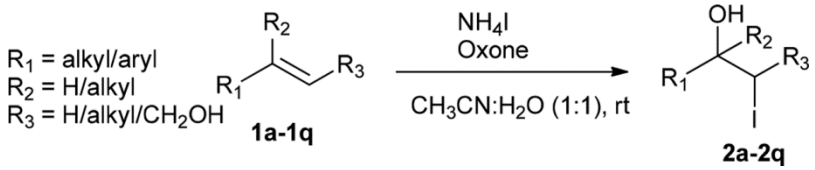
[c] Iodoformate product.

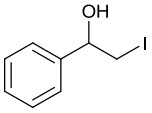
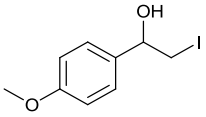
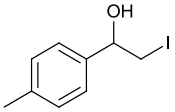
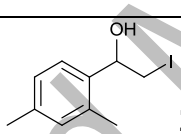
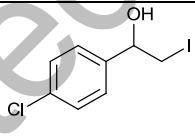
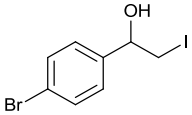
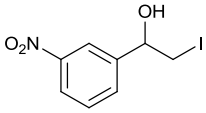
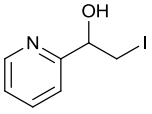
[d] Iodoacetate product.

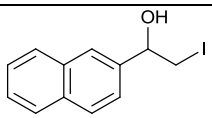
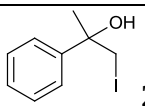
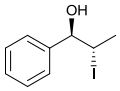
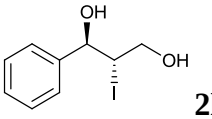
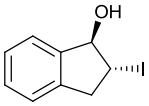
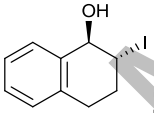
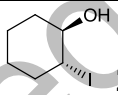
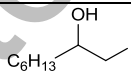
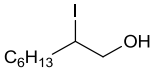
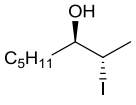
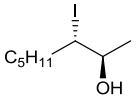
[e] Oxone® (0.614 g, 1 mmol).

[f] Oxone® (0.676 g, 1.1mmol).

Table 2. Synthesis of β-iodohydrins from olefins using NH_4I and oxone®[a]



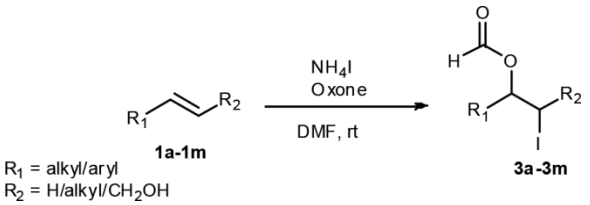
Entry	**Olefin**	Time (min)	Product	Yield[b] (%)
1	**1a**	10	 **2a**	99
2	**1b**	1	 **2b**	72
3	**1c**	8	 **2c**	95
4	**1d**	5	 **2d**	91
5	**1e**	15	 **2e**	90
6	**1f**	15	 **2f**	75
7	**1g**	60	 **2g**	78
8	**1h**	24[c]	 **2h**	00

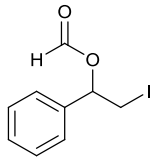
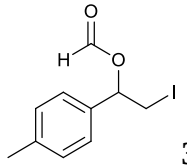
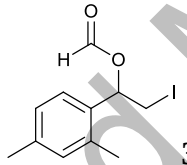
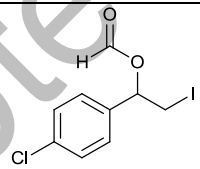
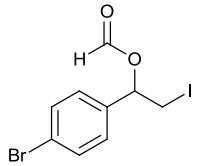
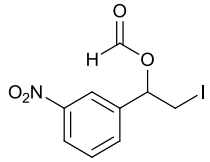
9	**1i**	10	 **2i**	80
10	**1j**	6	 **2j**	7
11	**1k**	5	 **2k**	84
12	**1l**	10	 **2l**	75
13	**1m**	5	 **2m**	95
14	**1n**	5	 **2n**	92
15	**1o**	2	 **2o**	93
16	**1p**	15	 **2p** (76%)	95
			 **2p[1]** (23%)	
17	**1q**	15	 **2q** (32%)	94
			 **2q[1]**(62%)	

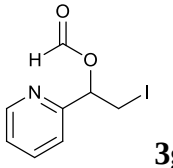
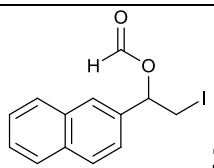
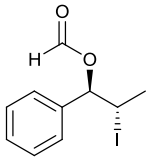
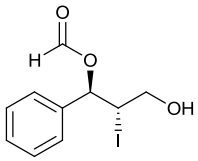
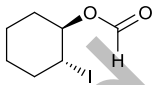
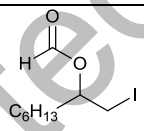
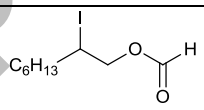
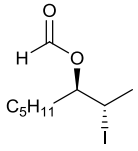
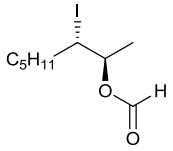
[a] Reaction conditions: substrate **1a-q** (1 mmol), NH_4I (0.160 g, 1.1 mmol), oxone® (0.461 g, 0.75 mmol), CH_3CN:H_2O (1:1) (10 mL), room temperature.

[b] Isolated yields. [c] 24 h.

Table 3. Synthesis of iodoformates from olefins using NH_4I and oxone®[a]



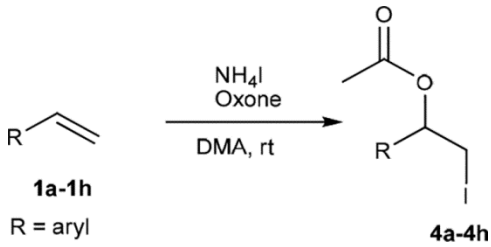
Entry	Olefin	Time (h)	Product	Yield[b] (%)
1	**1a**	4	 **3a**	96
2	**1b**	4	 **3b**	70
3	**1c**	4	 **3c**	75
4	**1d**	3	 3**d**	94
5	**1e**	3	 **3e**	93
6	**1f**	6	 **3f**	83

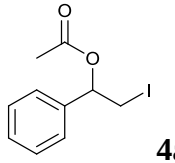
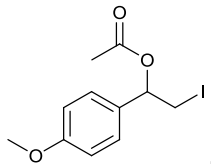
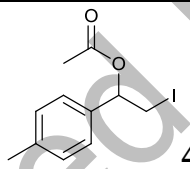
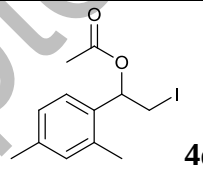
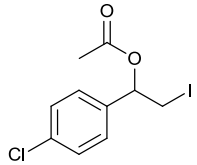
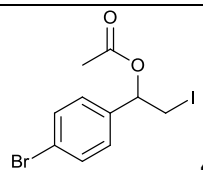
7	**1g**	20	 **3g**	90
8	**1h**	4	 **3h**	82
9	**1i**	4	 **3i**	79
10	**1j**	4	 **3j**	92
11	**1k**	4	 **3k**	94
12	**1l**	3	 **3l** (76%)	95
			 **3l**[1] (23%)	
13	**1m**	3	 **3m** (55%)	94
			 **3m**[1] (39%)	

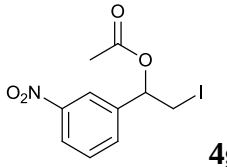
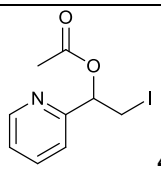
[a] Reaction conditions: substrate **1a-m** (1 mmol), NH_4I (0.160 g, 1.1 mmol), oxone® (0.676 g, 1.1 mmol), DMF (10 mL), room temperature.

[b] Isolated yields.

Table 4. Synthesis of iodoacetates from olefins using NH_4I and oxone®[a]



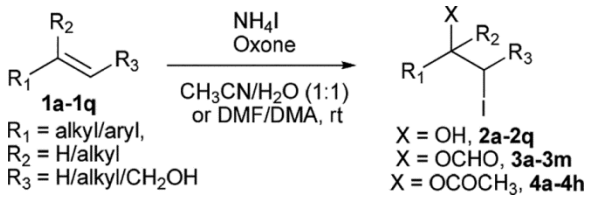
Entry	Olefin	Time (h)	Product	Yield[b] (%)
1	**1a**	4	 **4a**	70
2	**1b**	5	 **4b**	00 (91)[c]
3	**1c**	3	 **4c**	00 (84)[c]
4	**1d**	2	 **4d**	00 (91)[c]
5	**1e**	6	 **4e**	70
6	**1f**	7	 **4f**	72

7	**1g**	6	 **4g**	76
8	**1h**	20	 **4h**	88

[a] Reaction conditions: substrate **1a-h** (1 mmol), NH_4I (0.160 g, 1.1 mmol,), oxone® (0.676 g, 1.1 mmol), DMA (10 mL), room temperature.

[b] Isolated yields. [c] Iodohydrin products.

Scheme 1. Vicinal functionalization of olefins using NH_4I and oxone®.



Scheme 2. The plausible reaction mechanism.