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COMMUNICATION

Iodide Reagents Controlled the Reaction Pathway of Iodoperoxidation of alkenes: A High Regioselectivity Synthesis of α- and β-iodoperoxidates under Solvent-free Conditions†

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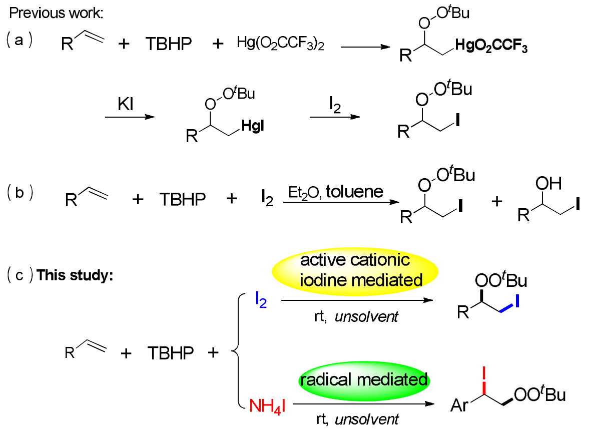
A highly atom-economical, efficient and environment-friendly iodoperoxidation of alkenes with TBHP and iodide/iodine is reported herein. This method afforded a convenient path to obtain two different configurations of iodoperoxidates from the same starting materials. Notably, the regiodivergent iodoperoxidation reaction was achieved by using of different iodide reagents. A series of control experiments were performed, which suggested the involvement of a radical pathway for the anti-Markovnikov type iodoperoxidates (α) in the combination of NH_4I/TBHP, and an active cationic iodine pathway for the Markovnikov type adduct (β) with I_2 and TBHP.

The simultaneous introduction of two different functional groups into the carbon-carbon double bonds of alkenes is an important fundamental process in organic synthesis.[1] Particularly, the regiodivergent difunctionalization reaction of alkenes is urgently desirable, since various molecular structures achieved.[2] Conventionally, the coupling reaction of alkene with an electrophile and a nucleophile is an efficient way to obtain the sole Markovnikov type adduct, due to the stabilization of carbocations.[3] Another observed regioselective reaction of alkene is the radical coupling reaction, and high regioselectivity of this type of reaction depends on the persistent radical effect.[4] Although steric hindrance of alkene structure could alter the regioselectivity type completely in the former reaction,[3b] it was still limited to some special substrates. In addition, only one type of adducts was formed in most of the reported difunctionalization reactions of alkenes. Therefore, controlling the regioselectivity in the difunctionalization reaction of alkenes remains a challenge.

The synthesis of iodoperoxidates has earned much attention in recent years, as the unique chemical and biological properties of peroxy and iodide groups.[5] The organic peroxides not only can serve as key reactive intermediates in diverse organic synthesis reactions, including oxidation, Kornblum-DeLaMare reactions, and epoxidation, but also can play important roles in the injury of cells, food safety, or medicinal chemistry as therapeutic drugs.[6] On the other hand, iodinated compounds have been recognised as important and versatile building blocks in organic synthesis, [7] which are valuable reagents in preparative nucleophilic substitution reactions occurring with retention of the peroxide fragment. Therefore, the simultaneous generation of iodide and peroxide moieties in the same molecule, may provide an easy access to compounds with pharmaceutical potential.



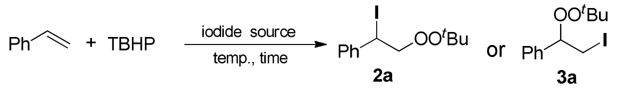
Scheme 1 Approaches to iodoperoxidation of alkenes

The method for the synthesis of iodoperoxidates was first reported in the 1970s, which was achieved through the peroxymercuration of alkenes followed by iodination (Scheme 1a).[8] Since then, the chemistry of iodoperoxidates compounds has developed rapidly, as its great potential for the design of new antimalarial drugs. Then the reaction of alkenes with 1,3-diiodo-5,5-dimethylhydantoin and hydrogen peroxide was reported.[9]

Recently, an iodine and hydroperoxides system were developed by Terent'ev and co-workers in the synthesis of vicinal iodoperoxidates (Scheme 1b).[5a, 10a] More recently, Zhu and co-workers reported the synthesis of 2-iodo-1-peroxidates□from styrenes and other olefins by using I_2 and TBHP at room tempereture in toluene.[10b] In contrast, these methods made progress in the used reagents. However, all the reported iodoperoxidates before were the Markovnikov-type iodo-containing adducts, to the best of our knowledge. No reports have been demonstrated for the synthesis of anti-Markovnikov type iodoperoxidates. Continued to our research interest in difunctionalization of alkenes,[11] herein we report a high atom economical and metal-free method for regioselectivity sythesis of α- and β- iodoperoxyalkanes under solvent-free reaction conditions (Scheme 1c).

At first, the iodoperoxidation of styrene **1a** and TBHP (in 70% aqueous) using 1.0 equiv of NIS as iodide source and MeCN as solvent at 80 °C for 10 h was performed. Fortunately , the target product **2a** was obtained in 10% yield under this reaction condition (Table 1, entry 1). Switching the iodide to KI did not raise the reaction efficiency. Interestingly, we found that decreasing the temperature resulted in a significant improvement of the yield of **2a** (Table 1, entries 2-3). When substituted Bu_4NI or NH_4I for KI, a further improvement of the yield to 93% (Table 1, entries 4-5). Lower amounts of NH_4I and shorten reaction time led to a slightly lower yield (90%; Table 1, entry 6). Different solvents such as EtOAc, DCM and DMF afforded the similar yields of **2a** (Table 1, entries 7-9). This indicated that the solvents had no effect on the product formation. Thus, we suspected that under solvent-free condition the iodoperoxidation of styrene with TBHP and NH_4I could also perform well. And it was confirmed by the 96% yield of **2a** under solvent-free. condition (Table 1, entry 10). To explore the role of iodide in this transformation, we replaced NH_4I with I_2. To our surprise, the **2a** product was not obtained but a regioisomer **3a** product generated (Table 1, entry 11). Decreasing the amount of iodine from 1 to 0.6 equiv, resulted in slightly lower yield (78%; Table 1, entry 12). Further swithching the solvents did not improve the

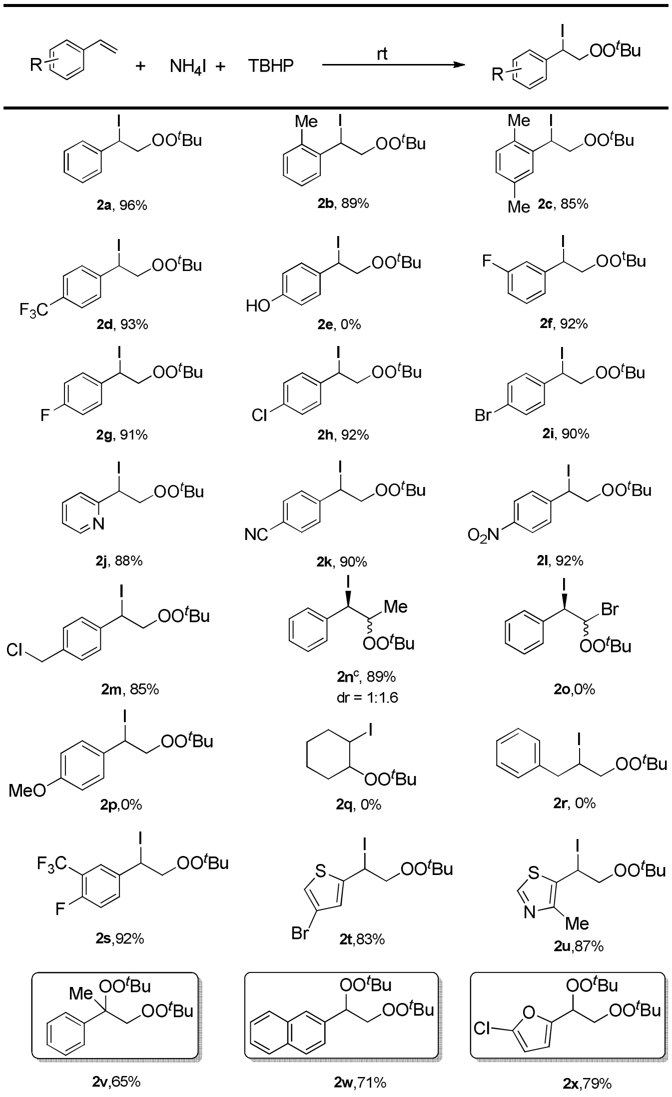
Table 1 Optimization of reaction conditions[a]



Entry	Iodide source (equiv.)	Solvent	Oxidant (equiv.)	Temp (°C) /time (h)	Yield(%)[b] 2a	3a
1	NIS (1.0)	MeCN	TBHP[c]	80/10	10	-
2	KI (1.0)	MeCN	TBHP[c]	80/10	16	-
3	KI (1.0)	MeCN	TBHP[c]	60/10	21	-
4	Bu_4NI (1.5)	MeCN	TBHP[c]	40/10	49	-
5	NH_4I (1.5)	MeCN	TBHP[c]	25/10	93	-
6[c]	NH_4I (1.1)	MeCN	TBHP[c]	25/4	90	-
7	NH_4I (1.1)	EtOAc	TBHP[c]	25/4	92	-
8	NH_4I (1.1)	DCM	TBHP[c]	25/4	94	-
9	NH_4I (1.1)	DMF	TBHP[c]	25/4	88	-
10	**NH_4I (1.1)**	**--------**	**TBHP[c]**	**25/4**	**96**	**-**
11	I_2 (1.0)	DCM	TBHP[c]	25/4	-	80
12	I_2 (0.6)	Et_2O	TBHP[c]	25/4	-	78
13	I_2 (0.6)	DMF	TBHP[c]	25/4	-	75
14	I_2 (0.6)	MeCN	TBHP[c]	25/4	-	73
15	I_2 (0.6)	---------	TBHP[c]	25/4	-	75
16	I_2 (0.6)	MeCN	TBHP[d]	25/4	-	95
17	I_2 (0.6)	---------	TBHP[d]	25/4	-	89
18	I_2 (0.6)	---------	TBHP[d]	80/2	-	-
19[e]	**I_2 (0.6)**	**---------**	**TBHP[d]**	**25/2**	**-**	**98**

[a] Reaction conditions: Styrene (1 mmol), TBHP (5.8 mmol), Solvent (2 mL). [b] Yield determined by NMR analysis using an internal standard. [c] TBHP (70% aqueous solution, 5.8 mmol). [d] TBHP (6.7 M TBHP in decane, 3.6 mmol).

Table 2 Scope of styrenes for the synthesis of α-iodoperoxidates[a,b]



[a] Reaction conditions: styrene (1.0 mmol), NH_4I (1.1 mmol), and TBHP (5.8 mmol, 70% aqueous solution) were stirred at 25 °C for 4 h. [b] Isolated yield. [c] *trans-β*-Methylstyrene was used as substrate.

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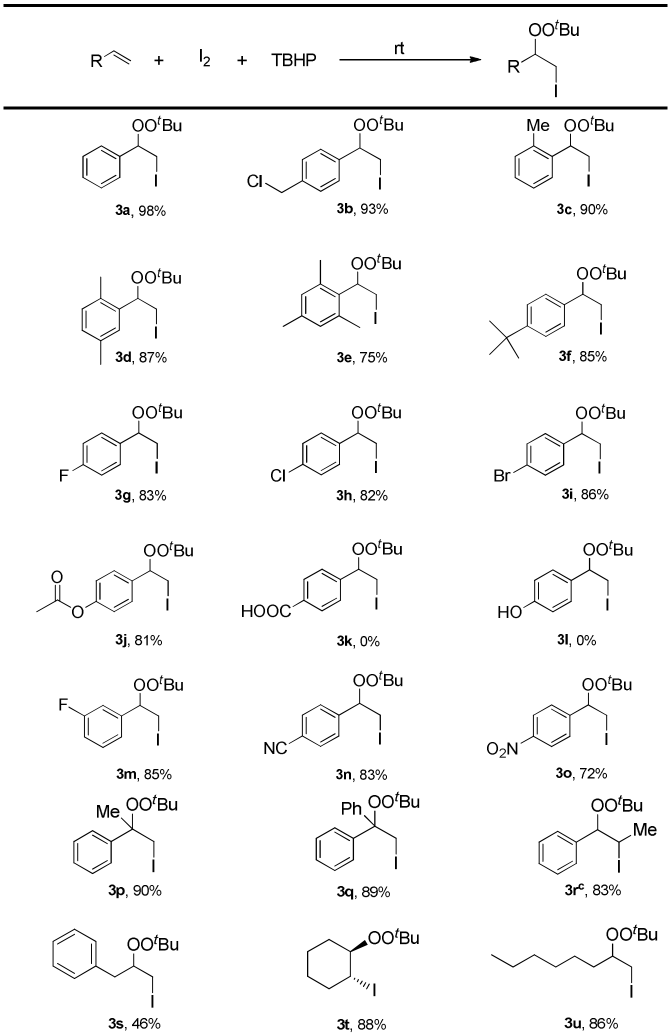
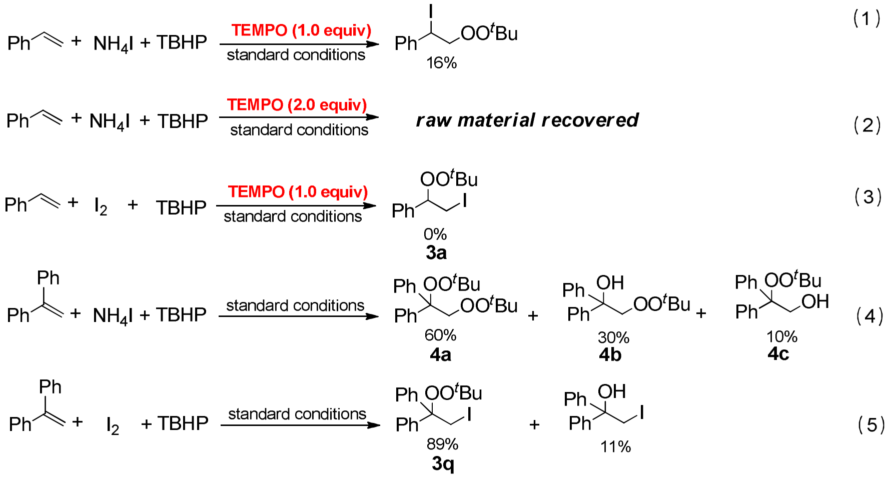
Table 3 Scope of alkenes for the synthesis of β-iodoperoxides[a,b]



[a] Reaction conditions: styrene (1.0 mmol), I_2 (0.6 mmol) and TBHP (3.6 mmol, 6.7 M TBHP in decane) were stirred at 25 °C for 2 h. [b]Isolated yield. [c] *trans-β*-Methylstyrene was used as substrate.

yield of **3a**, since the byproduct 2-iodo-1-phenylethanol was always produced. When changing the aqueos TBHP (in 70% aqueous) to nonaqueous TBHP (6.7 M TBHP in decane), the yield of **3a** dramatically increased to 95%. However, when reaction temperature further increased and reaction time shortened, the amount of **3a** decreased, due to the transformation of **3a** into 2-iodo-1- phenylethanone. Therefore, the optimal conditions for **2a** and **3a** were those described in entry 10 and 19.

Under the optimal conditions, a wide range of styrenes **1** were investigated to evaluate the efficiency and substrates scope of this novel protocol for the synthesis of α-iodoperoxidates (Table 2). In general, the reaction tolerated a wide range of substituted aryl alkenes to give the corresponding α-iodoperoxidates in excellent yields (Table 2, entries **2a-2n**). It is noted that styrenes bearing electro-withdrawing groups (4-NO_2, 3-F and 1-F-2-CF_3) gave the disired products in higher yields than those bearing electro-donating groups (2-Me or 2,5-dimethyl) on the phenyl ring (Table 2, entries **2b-2d, 2f, 2l** and **2s**). Styrenes with diverse functions were well tolerated, granting entry for further functionalization. Styrene with halogen substituents provided the products in good yields of 90-92% (**2f-2m**). Other functional motifs such as trifluoromethyl, cyano and nitro group on the styrene remained intact and the corresponding α-iodoperoxidates were isolated in 93%, 90% and 92% (**2d**, **2k**, **2l**) respectively. However, neither did the reaction with 4-hydroxystyrene **1e** nor 4-methoxystyrene **1p** worked, but a large amount of black precipitation formed after the reaction. Moreover, vinyl substituted aromatic compounds such as pyridine, thiophene and thiazole were also suitable for the α-iodoperoxidation reaction, thus providing good yields of the corresponding products (**2j, 2t** and **2u**). Furthermore, the optimized reaction conditions was also successful for internal styrene *trans*-β-methylstyrene **1n**, forming the desired product **2n** in high yield with a diastereoselective ratio 1:1.16. However, *trans*-β-bromostyrene **1o**, failed to give the corresponding product. Similarly, aliphatic olefin such as cyclohexene **1q** or enven the nonconjugated olefin allylbenzene **1r** were completely unreactive, these results show that a resonance stabilizing group on the olefin is beneficial. It was noteworthy that



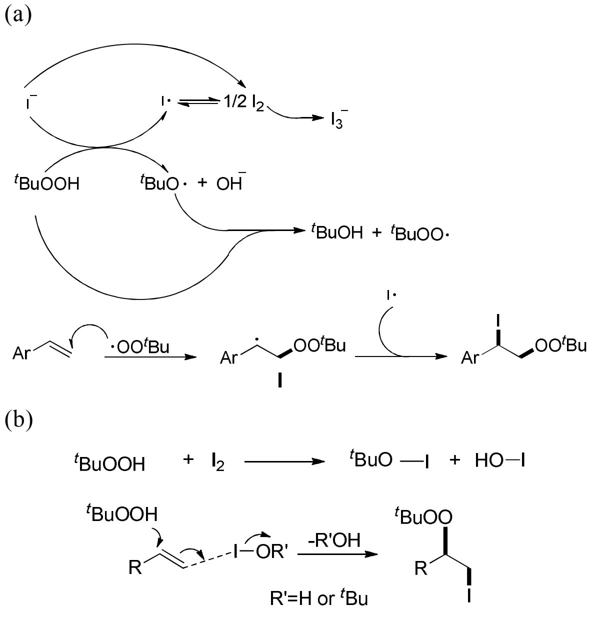
Scheme 2 Control experiments for the reaction mechanism

when α-Methylstyrene **1v,** vinylnaphthalene **1w** and 2-chloro-5-vinylfuran **1x** were used as substratea, diperoxidate products rather than the α-iodoperoxidate were obtained.

Subsequently, the olefin scope for the synthesis of β-iodoperoxidates was explored using nonaqueous TBHP and I_2 as the standard coupling partner (Table 3). In general, all styrenes with either electro-donating or electron-withdrawing substituents afforded products in good yields (Table 3, entries **3a-3o**). However, 4-vinylbenzoic acid and 4-vinylphenol did not form the desired products. This reaction gave good yields for α- and β-substituted styrenes (Table 3, entries **3p-3r**). Notably, the method was also proved to be applicable to aliphatic olefins. When cyclohexene and oct-1-ene were used as substrate, the desired iodoperoxide **3t** and **3r** were obtained in 88% and 86% yields, respectively, under solvent-free reaction condition.

To gain insight into the reaction mechanism, several control experiments were performed. When 1.0 equiv of TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy), a well-known radical inhibitor, was added to the reaction mixture of syrene, NH_4I, and TBHP, the yield of **2a** decreased from 96% to 16% (Scheme 2, eqn(1)). When 2.0 equiv of TEMPO was added, the reaction was completely halted (Scheme 2, eqn(2)). While in the standard condition, no **3a** product was obtained, after 1.0 equiv of TEMPO was added (Scheme 2, eqn(3)). Notably, a high amount of 1,2-bis (*tert*-butylperoxy) ethyl) benzene **4a** and 2-(*tert*-butylperoxy)-1-phenylethanol **4b** were isolated, when ethene-1,1-diyldibenzene was employed under the standard reaction conditions (Scheme 2, eqn (4)). These findings offered convincing evidence for the addition of ^{t}BuOO• radical to the double bond of styrene. The ^{t}BuOO• radical was generated from the redox reaction between NH_4I and TBHP. However, in the same condition, the β-iodoperoxidate **3q** and β-iodo-1,1-diphenylethanol were formed especially, when replacing NH_4I with I_2 (Scheme 2, eqn (5)). In addition, the experimental results of the olefin scope for the synthesis of α- and β-iodoperoxidates indicated that different reaction mechanisms existed between NH_4I/TBHP and I_2/TBHP reaction systems with following reasons: (i) different reactivities of aliphatic olefins (Table 2, entries **2q, 2r** & Table 3, entries **3s-3u**); (ii) different products of α-substituted alkenes (Table 2, entry **2p** & Table 3, entry **3p**; Scheme 2, eqn (4) & (5)); (iii) different configurations of product with β-substituted alkenes in the two different reaction condition (Table 2, entry **2n** & Table 3, entry **3r**); (iv) only the *trans* product was formed from cyclohexene (Table 3, entry **3t**).

On the basis of the above results and reports in literatures,[12] two plausible mechanisms for the formation of α- and β-iodoperoxidates are proposed (Scheme 3). In the reaction condition of NH_4I and TBHP for the synthese of α-iodoperoxidate (Sheme **3a**), first, the *tert*-butoxyl radical and iodine radical formed.[13] Then, the *tert*-butoxyl radical abstracts a hydrogen from TBHP to generate *tert*-butylperoxyl radical. The persistent radical ^{t}BuOO· is then immediately trapped by styrene, leading to the formation of the benzylic radical intermediate **I**. Finally, the rapid combination of I· and intermediate **I** results in the α-iodoperoxidate product. Although Zhu et al. proposed a radical mechanism for the formation of β-iodoperoxidates in their work[10b], based on our reaction results, an active cationic iodine mechanism is presented in Scheme **3b** for the formation of β-iodoperoxidates with I_2 and TBHP.[14] Initially, iodine reacts with TBHP and generates the reactive hypoiodite acid and ^{t}BuOI,[14a,b] which coordinates with styrene at the β-C position and polarizes the carbon-carbon double bond. This is followed by nucleophilic attack of ^{t}BuOOH on α-C-atom to generate the β-iodoperoxidate and elimination of H_2O or ^{t}BuOH. ^{t}BuOOH plays dual roles in these transformation, acting as an oxidant to increase the electrophilicity of the elemental iodine in the first step and as a nucleophile in the second step. Conversion of both iodine atoms of I_2 into the final product resulted in 100% iodine atom economy for iodoperoxidation of alkenes reaction.



Scheme 3 Suggested mechnisms of products formation

One could argue that why the formation of β-iodoperoxidates were totally halted in the combination of NH_4I/TBHP reaction system, since the formation of I_2 during the redox reaction between NH_4I and TBHP. This may be attributed to the fact that, I_3^- exists rather than I_2 in abundance of iodide ion,[15] thus exclude continued oxidation by TBHP to form the the reactive hypoiodite acid or ^{t}BuOI. Therefore, the combination of NH_4I/TBHP provides the sole anti-Markovnikov type iodoperoxidate.

Conclusions

In conclusion, we have successfully developed a highly atom-economical, environment-friendly, and efficient method for synthesis of α- and β-iodoperoxidates with TBHP and iodide/iodine under solvent-free reaction conditions. By varying the iodide reagents, the reaction conditions can be fine-tuned to regioselective synthesis of α-iodoperoxidates and β-iodoperoxidates. The excellent regioselectivity for the anti-Markovnikov type iodoperoxidates (α-iodoperoxidates) depended

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on the persistent radical effect while the exclusive formation of Markovnikov type iodoperoxidates (β-iodoperoxidates) was attributed to the formation of a more stable carbocation intermediate. The reactions have broad substrate scope, mild reaction conditions, and high functional group tolerance. Investigation of the detailed reaction mechanism and potential medicinal activities is underway in our laboratory.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Detailed experimental procedures, characterization of products, and NMR spectral charts. See DOI: 10.1039/b000000x/

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Graphical Abstract

A highly atom-economical, efficiency and environment-friendly iodoperoxidation of alkenes with TBHP and iodide/iodine is reported.