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An aqueous medium-controlled stereospecific oxidative iodination of alkynes: efficient access to (*E*)-diiodoalkene derivatives†‡

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A new and versatile approach for the stereospecific iodination of alkynes using cheap, air stable and non-toxic reagents in aqueous media has been developed. This protocol is tolerant of various functional groups, and provides a broad range of vicinal diiodoalkenes with exceptional *E*-selectivity under mild conditions. Scale-up reactions (up to 5 g) established the proficiency of this protocol and highlight the feasibility of large scale reactions.

The control of the chemical reactivity of a substance to produce a product selectively among a series of distinct valuable possible products is a highly attractive concept in organic chemistry.[1] Since the seminal discovery of enhanced rates and selectivities of Diels–Alder reactions in water by Breslow[2] and Grieco[3] in the early 1980's, aqueous organic chemistry has experienced exponential growth.[4] In most of the cases, due to hydrophobic effects, the rates and selectivities of the reactions have been enhanced to a greater extent even though the reactants are sparingly soluble or insoluble in aqueous media. Besides this, water is an inexpensive, safe, readily available and ideal green solvent, which can potentially provide benefits for chemical synthesis in terms of resource economy, energy efficiency, health and environmental safety.

The selective and controlled introduction of an iodine atom into small organic molecules has attracted considerable attention among the scientific community due to their broad range of applications as key intermediates and valuable synthons in synthetic organic chemistry[5] and as useful medical diagnostics[6] such as radioactively labeled markers or contrast agents. In particular, 1,2-diiodoalkenes signify one important subclass of organo iodine compounds frequently used in organic synthesis.[7] They have attracted significant attention due to their key roles in a wide range of functional group transformations and metal-catalysed homo- and cross-coupling reactions for developing new carbon–carbon bonds.[8,9] Furthermore, the 1,2-diiodovinyl substrates are valuable precursors for many heterocycles and key building blocks for naturally occurring bioactive compounds.[10] For instance, 1,3-enyne entities, which can be easily accessed from 1,2-diiodovinyl compounds, are found in many naturally occurring and biologically active compounds such as calichemicin γ1. In addition, they exhibit distinct biological activities which include antitumor, antibiotic and terbinafine, and also serve as potent drugs for superficial fungal infections.[10]

Owing to their broad applicability in chemical synthesis, several methods have been developed for their preparation. The most straightforward method for stereospecific di-iodination is the direct addition of iodine to alkynes;[11] however, these reactions proceed slowly and the conversion of the reaction is very low. The majority of vicinal (*E*)-diiodoalkenes are prepared using I_2–Al_2O_3, ICl–NaI and bis(pyridine)iodonium(I) tetrafluoroborate in the presence of iodide ions.[12–14] These systems enhanced the productivity of the reaction but had other problems like purification, use of costly reagents and environmental concerns associated with the use of organic solvents as the reaction media and hazardous elemental iodine. The other convenient approach for the synthesis of *trans*-diiodoalkene synthons is oxidative iodination. Although the oxidative iodination of alkynes offers an efficient, eco-friendly and synthetically useful means of fabricating iodo-functionalized molecules, most of the reported protocols suffer from the use of acidic additives, metal oxidants and hypervalent iodine reagents, the requirement of specific reaction temperatures, poor selectivity of the iodination products, low to moderate yields, limited scope of the reaction and use of organic solvents as the reaction medium (Scheme 1a).[15] In particular, the exclusive formation of 1,2-*trans*-diiodoalkenes through an oxidative iodination protocol in environmentally benign conditions is quite elusive and signifies a formidable synthetic challenge. Therefore, the development of efficient, safer, sustainable and high yielding strategies for the stereospecific

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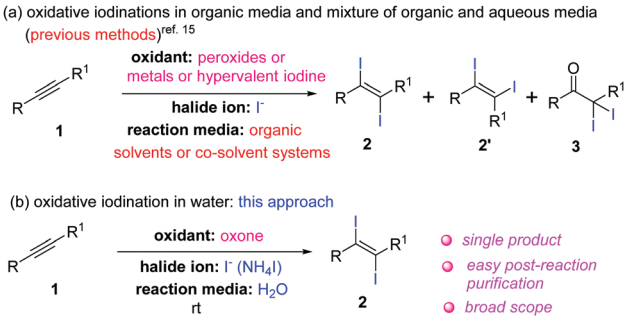


Scheme 1 Previous approaches and our method towards oxidative diiodination of alkynes.

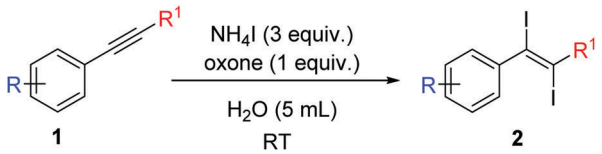
diiodination of alkynes is still attracting the interest of synthetic organic chemists.

In continuation of our research programme to develop novel methodologies which exploit eco-friendly solvents and reagents,[16] herein, we wish to describe a simple, efficient and environmentally benign protocol for a highly stereospecific oxidative (*E*)-diiodination of alkynes at room temperature in aqueous media. In this procedure, we employed stable, easy-to-handle and inexpensive inorganic salts such as NH_4I (iodide source) and oxone (oxidant) as reagents (Scheme 1b). Since the deoxygenated by-products generated during the reaction from oxone can be easily removed by water,[17] the post-reaction purification of the products is much easier than for the other methods which employ hypervalent iodine reagents or other organic oxidants.

We have initiated our investigation by choosing phenylacetylene (**1a**) as a model substrate and performed its iodination reaction in aqueous media under oxidative iodination conditions using NH_4I as an iodide source and oxone as an oxidant (Table S1, ESI‡). To our surprise, the reaction of **1a** with 2 equiv. of NH_4I and 1 equiv. of oxone in water provided the desired product **2a** in 88% yield with exclusive *E*-selectivity within a short reaction time at room temperature (entry 1, Table S1, ESI‡). This reaction encouraged us to optimize the reaction conditions to achieve the desired (*E*)-(1,2-diiodovinyl)benzene (**2a**) in better yields. In this context, initially, we tested the model reaction by increasing or decreasing the molar ratios of the reagents, which revealed that 3 equiv. of NH_4I and 1 equiv. of oxone with respect to **1a** is optimum for obtaining **2a** in the highest yield with the same selectivity (entry 2, Table S1, ESI‡). Finally, several oxidants were screened in the reaction by replacing oxone with $K_2S_2O_8$, *m*-CPBA, aq. H_2O_2 and aq. TBHP. The oxidative iodination of **1a** with $K_2S_2O_8$ provided the product **2a** in 30% yield after 20 min of reaction time, while prolonging the reaction time to 1 h gave the product in 93% yield (entry 7, Table S1, ESI‡). The other oxidants like *m*-CPBA, aq. H_2O_2 and aq. TBHP furnished the desired product in low to moderate yields even after increasing the reaction times to 24 h (entries 8–10, Table S1, ESI‡). It is worth mentioning that, even though all the oxidants examined in this study delivered the exclusive *E*-selective product **2a** with NH_4I as the iodide ion source, oxone is the best suited oxidizing agent to obtain the highest yield of **2a**. Furthermore, it is reported that the oxidative iodination of alkynes **1** with the oxone/KI reagent system in CH_3CN–H_2O co-solvent reaction media yielded a mixture of vicinal diiodoproducts **2** and oxyhalogenated α,α′-diidoketones **3** (Scheme 1a).[15c] However, the present reagent system (oxone/NH_4I) in aqueous media led to the formation of the *trans* diiodoalkene as the sole product.

With the optimized conditions in hand, we investigated the generality of the reaction with a variety of alkynes in aqueous media (Tables 1 and 2). First, the scope of various aromatic alkynes was explored (Table 1). The methyl substituted aromatic alkynes **1b–1d** gave the corresponding products **2b–2d** in excellent yields irrespective of the position of the methyl group on the phenyl ring (entries 2–4, Table 1). The *para n*-pentyl and *tert*-butyl substituted alkynes **1e** and **1f** gave the desired *E*-diiodo products **2e** and **2f** in 87 and 94% yields (entries 5–6, Table 1), respectively. The *ortho* methoxy and *para* phenoxy substituted alkynes **1g** and **1i**, respectively, provided exclusively the corresponding transdiiodo products **2g** and **2i** both in 90% yield (entries 7 and 9, Table 1). Whereas, the *para* methoxy substituted aromatic alkyne **1h** yielded the vicinal diiodoalkene in 92% yield with 3.18 : 1 ratio of the *E* and *Z* isomers (**2h** and **2h′**) (entry 8, Table 1). The halo functional groups F, Cl and Br were well tolerated under the present reaction conditions and the phenyl acetylenes **1j–1m** furnished the respective products **2j–2m** in good to excellent yields at room temperature (entries 10–13, Table 1).

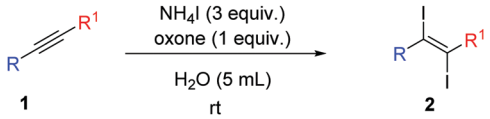
Table 1 Scope of the reaction[a,b]

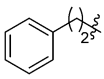


Entry	Alkyne **1**	Product **2**: time, yield
1	R = R^1 = H; **1a**	**2a**: 20 min, 97%
2	R = 2-Me, R^1 = H; **1b**	**2b**: 20 min, 98%
3	R = 3-Me, R^1 = H; **1c**	**2c**: 25 min, 96%
4	R = 4-Me, R^1 = H; **1d**	**2d**: 20 min, 98%
5	R = 4-*n*-Pe, R^1 = H; **1e**	**2e**: 01 h, 87%
6	R = 4-*t*-Bu, R^1 = H; **1f**	**2f**: 30 min, 94%
7	R = 2-OMe, R^1 = H; **1g**	**2g**: 10 min, 90%
8[c]	R = 4-OMe, R^1 = H; **1h**	**2h**: 05 min, 70%
9	R = 4-OPh, R^1 = H; **1i**	**2i**: 01 h, 90%
10	R = 2-F, R^1 = H; **1j**	**2j**: 3.5 h, 98%
11	R = 3-F, R^1 = H; **1k**	**2k**: 4.0 h, 98%
12	R = 4-F, R^1 = H; **11**	**21**: 20 min, 94%
13	R = 3-CI, R^1 = 1-1; **1m**	**2m**: 5.0 h, 88%
14	R = 4-Br, R^1 = H; **1n**	**2n**: 12 h, 55%
15[d]	R = 4-Br, R^1 = H; **1n**	**2n**: 3 h, 85%
16	R = 4-CF_3, R^1 = H; **1o**	**2o**: 6.0 h, 90%
17	R = 4-CO_2Me, R^1 = H; **1p**	**2p**: 24 h, 00%
18[d]	R = 4-CO_2Me, R^1 = H; **1p**	**2p**: 5 h, 95%
19	R = 4-NO_2, R^1 = H; **1q**	**2q**: 24 h, 00%
20[d]	R = 4-NO_2, R^1 = H; **1q**	**2q**: 24 h, 98%
21	R = H, R^1 = Me; **1r**	**2r**: 50 min, 91%
22	R = H, R^1 = Et; **1s**	**2s**: 1.5 h, 90%
23	R = H, R^1 = *n*-Bu; **1t**	**2t**: 3 h, 80%

[a] Unless otherwise mentioned, alkyne **1** (1 mmol), NH_4I (3 mmol), oxone (1 mmol) and water (5 mL) were used at room temperature. [b] Isolated yields. [c] The *cis* vicinal diiodo product **2h′** was isolated in 22% yield along with **2h**. [d] Reaction performed at 60 °C.

Table 2 Scope of hetero aromatic and aliphatic alkynes[a,b]



Entry	Product 2 (time, yield)	Entry	Product 2 (time, yield)
1	**2u**: R^1 = H, R =  (24 h, 84%)	5	**2y**: R^1 = H, R =  (3 h, 96%)
2	**2v**: R^1 = H, R =  (24 h, 87%)	6	**2z**: R^1 = H, R =  (3 h, 92%)
3	**2w**: R^1 = H, R =  (12 h, 95%)	7	**2aa**: R^1 = H, R =  (2 h, 89%)
4	**2x**: R^1 = H, R =  (1 h, 96%)	8	**2ab**: R^1 = CH_3, R = C_5H_{11} (0.66 h, 96%)
		9	**2ac**: R^1 = R = C_3H_7 (2 h, 95%)

[a] The reactions were performed using alkyne **1** (1 mmol), NH_4I (3 mmol), oxone (1 mmol) and water (5 mL) at room temperature. [b] Isolated yields.

However, the Br substituted alkyne **1n** exhibited somewhat slower reactivity than F and Cl substituted phenyl acetylenes at room temperature to give 55% yield of **2n** and enhanced reactivity at 60 °C with 85% yield (entries 14–15, Table 1).

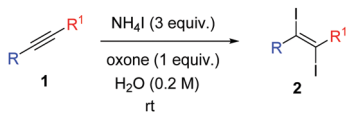
The CF_3 substituted phenyl acetylene **1o** endured oxidative iodination conditions to afford 90% of **2o** within 6 h of reaction time at room temperature (entry 16, Table 1). The strong electron withdrawing group substituted aromatic alkynes **1p** and **1q** did not react at room temperature, but they gave the corresponding products **2q** and **2p** in 95 and 98% yields, respectively, at the reaction temperature of 60 °C (entries 17–20, Table 1). The 1,2-disubstituted alkynes **1r–1t** reacted smoothly under the present reaction conditions to provide the desired products **2r–2t** in 80–91% yields (entries 21–23, Table 1).

To further extend the scope of the reaction, we investigated the hetero aromatic and aliphatic (terminal and internal) alkynes under the optimized conditions (Table 2). We found that the rates of the reactions of the hetero aromatic alkynes **1u** and **1v** were slower than that of the aromatic alkynes and delivered the respective products **2u** and **2v** in 84% and 87% yields, respectively (entries 1–2, Table 2). The iodination reactions of aliphatic alkynes **1w–1z** and **1aa–1ac** underwent smoothly under the present reaction conditions to give the corresponding products **2w–2z** and **2aa–2ac** in good to excellent yields (entries 3–9, Table 2).

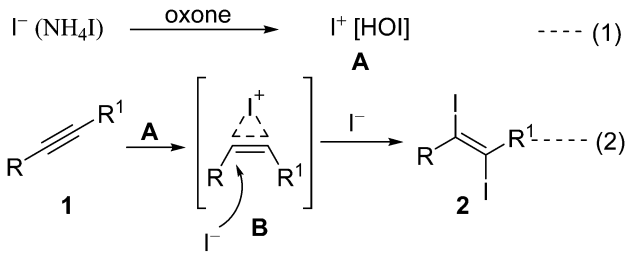
After evaluating the scope of the reaction, we then turned our attention to enhancing the synthetic viability of the present method. In connection with this, we attempted gram scale reactions of the selected examples (**1a**, **1w**, **1x** and **1ac**) and remarkably obtained the corresponding stereospecific (*E*)-diiodo products in excellent yields (entries 1–4, Table 3). Inspired by these results, we further performed the scale up reactions up to 5 gram scale. These large scale reactions also provided the corresponding products in slightly lower yields with prolonged reaction times compared to the 1 mmol scale reactions (entries 5–8, Table 3). However, the selectivity of the products is consistent with the 1 mmol scale reactions. These reactions highlighted the synthetic proficiency and viability of large scale experiments.

A plausible reaction mechanism for the oxidative iodination of alkynes using NH_4I and oxone has been depicted in Scheme 2. Initially, it is assumed that oxone may oxidize iodide ions to electrophilic iodine species **A**.[16e] This reactive species **A** may react with alkyne **1** to form a transient cyclic iodonium species **B**. The unstable intermediate **B** may undergo nucleophilic attack by I^- available *in situ* from the opposite side of the cyclic iodonium ion to form the desired *trans*-diiodo alkene **2**.

Table 3 Large scale experiments



Substrate **1**	Product **2**: time, yield	Substrate **1**	Product **2**: time, yield
One-gram scale		Five grams scale	
1 R = Ph, R′ = H; **1a** 10 mmol (1.021 g)	**2a**: 0.83 h, 96% (3.417 g)	5 R = Ph, R′= H; **1a** 50 mmol (5.106 g)	**2a**: 2 h, 93% (16.551 g)
2 R = $C_6H_5CH_2CH_2$, R′ = H; **1w** 09 mmol (1.170 g)	**2w**: 14 h, 95% (3.283 g)	6 R = $C_6H_5CH_2CH_2$ R′ = H; **1w** 39 mmol (5.077 g)	**2w**: 24 h, 89% (13.328 g)
3 R = *n*-Pentyl, R′ = H; **1x** 11 mmol (1.057 g)	**2x**: 3.5 h, 92% (3.541 g)	7 R = *n*-Pentyl, R′ = H; **1x** 53 mmol (5.097 g)	**2x**: 6 h, 89% (16.508 g)
4 R = R′ = *n*-Pr; **1ac** 10 mmol (1.102 g)	**2ac**: 2.5 h, 94% (3.421 g)	8 R = R′ = *n*-Pr; **1ac**; 46 mmol (5.069 g)	**2ac**: 6 h, 90% (15.070 g)



Scheme 2 Plausible reaction mechanism for the oxidative iodination of alkynes.

Conclusions

In conclusion, we have developed an efficient and mild approach for the synthesis of *trans*-diiodoalkenes from alkynes in a highly selective manner under oxidative iodination conditions. This method operates under mild conditions and employs cheap, commercially available and non-toxic inorganic salts as reagents and water as a green solvent. The scope of the reaction has been demonstrated with various alkynes such as aromatic, aliphatic and hetero aromatic alkynes. Furthermore, the synthetic practicability of the method has been established by performing gram-scale experiments (up to 5 g scale) under standard conditions.

Conflicts of interest

There are no conflicts to declare.

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