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Hypoiodite-Catalyzed Regioselective Oxidation of Alkenes: An Expeditious Access to Aldehydes in Aqueous Micellar Media

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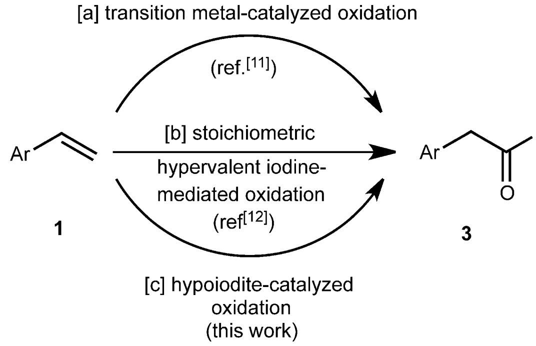
Abstract: A highly anti-Markovnikov selective oxidation of alkenes based on *in situ* generated hypoiodite catalysis in aqueous micellar media under mild conditions has been described. This novel catalytic system realizes an efficient synthesis of aldehydes from alkenes in an economically viable and environmentally safe fashion. The preliminary mechanistic studies suggest that the reaction proceeds *via* tandem iodofunctionalization/1,2-aryl or alkyl migration. The scope and limitations of this tandem process are demonstrated with various mono- and disubstituted (terminal and internal) olefins.

Keywords: aldehydes; hypoiodite catalysis; micelles; oxidation; regioselectivity

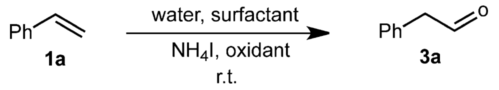
With the increased environmental consciousness, achieving organic transformations in aqueous media under mild conditions is of great importance in modern synthetic chemistry and paves the way to design green, safe and economically viable processes. Despite the inherent advantages of water, such as readily availability, non-toxicity, non-flammability, cheapness and safe handling, over organic solvents,[1] its use as reaction medium has constraints due to the poor solubility of most organic substances. This solubility issue can be overcome by using surfactants which form nanometer micelles (nanoreactors) by self-aggregation in water.[2] Over the past few years, the use of surfactants in aqueous reactions has received considerable attention from synthetic chemists owing to their ability to not only increase the solubility of organic substrates but also the selectivity and reactivity of a reaction.[3]

Aldehydes are valuable precursors,[4] versatile intermediates in target oriented organic synthesis[5] and essential ingredients in the manufacture of flavours, soaps and perfumes.[6] Traditional processes for aldehyde preparation rely on the oxidation of primary alcohols. Generally, these methods require prior synthesis of alcohols from terminal olefins which is a critical process.[7] The current approaches for aldehyde production from C-C multiple bonds are hydroformylation of alkenes and hydration of alkynes. But, the hydroformylation provides homologous aldehydes and the anti-Markovnikov hydration of alkynes frequently utilizes metal-based catalysts.[8] As the terminal alkenes are attractive starting materials and key intermediates for many reactions, their direct oxidative transformation to methyl ketones on the basis of Markovnikov's rule, known as Tsuji–Wacker oxidation, has been broadly adapted in both academia and industry.[9] However, in contrast, the aldehyde selective oxidation (without the cleavage of C=C double bond) of terminal olefins has represented a formidable synthetic challenge for many decades.[10] Recently, significant efforts have been made to address the historical challenge of selective anti-Markovnikov functionalization of terminal olefins to aldehydes, that led to diverse metal-based catalytic systems (Scheme 1a).[11] However, most of them require relatively costly metals with some degree of toxicity, complex ligands, hazardous solvents and harsh reaction conditions. Alternatively, a few metal-free protocols have appeared in the literature which utilize hypervalent iodine compounds in stoichiometric amounts and strong acids as additives (Scheme 1b).[12] But, the use of stoichiometric hypervalent iodine compounds generates equimolar amounts of organic waste. Thus, the development of simple, safer and sustainable strategies for the anti-Markovnikov selective oxidation of alkenes under



Scheme 1. Different strategies for the anti-Markovnikov selective oxidation of vinylarenes.

Table 1. Optimization study for the regioselective oxidation of styrene (**1a**) to phenylacetaldehyde (**3a**).[a,b]



Entry	NH_4I (mol%)	Oxidant (equiv.)	Surfactant (mol%)	Time [h]	Yield [%]
1	20	oxone (1)	N/A[c]	2.5	43
2	20	N/A[c]	N/A[c]	5	00
3[d]	N/A[c]	oxone (1)	N/A[c]	24	trace
4	20	oxone (1)	SDS (20)	0.25	83
5	20	oxone (1)	CTAB (20)	1	48
6	20	oxone (1)	3PP[e] (20)	1	58
7	20	oxone (1)	TWEEN® 80 (20)	2	51
8	20	$K_2S_2O_8$ (1)	SDS (20)	24	00
9	20	*m*-CPBA (1)	SDS (20)	24	18
10	20	aq. H_2O_2 (1)	SDS (20)	24	00
11	20	aq. TBHP (1)	SDS (20)	24	00
12	20	oxone (1)	SDS (30)	0.13	93
13	20	oxone (1)	SDS (40)	0.1	93
14	10	oxone (1)	SDS (30)	0.25	81
15	30	oxone (1)	SDS (30)	0.11	93
16	20	oxone (1.5)	SDS (30)	0.08	66
17	20	oxone (0.75)	SDS (30)	0.58	88
18[f]	20	oxone (1)	SDS (30)	0.13	68

[a] *Reaction conditions:* styrene (1 mmol), NH_4I, oxidant, surfactant, water (10 mL), room temperature.
[b] Isolated yields (as 2,4-DNP derivative **4a**).
[c] N/A refers to not applicable.
[d] 1-Phenylethane-1,2-diol was observed.
[e] 3PP = 3-(1-pyridinio)-1-propanesulfonate.
[f] 5 mL of water were used as solvent.

mild conditions is highly desirable and presents a significant challenge to research.

In recent years, hypoiodite-catalyzed oxidative transformations have emerged as an attractive area of research.[13] However, to the best of our knowledge, there are no reports on hypoiodite-mediated catalytic oxidation of alkenes in an anti-Markovnikov fashion. Herein, we describe a novel and efficient method for the highly regioselective oxidative functionalization of olefins using stable, inexpensive and easy-to-handle reagents, such as NH_4I as iodine containing precatalyst and oxone as terminal oxidant, in presence of aqueous SDS self-organized nanoreactors at room temperature.

Initially, we anticipated the regioselective oxidation of vinylarenes through the activation of C=C double bond with *in situ* generated electrophilic iodine species in aqueous media. To test our hypothesis, we have chosen styrene as a model substrate and investigated its reaction with NH_4I (as precatalyst) and oxone (as terminal oxidant) in water. The reaction of styrene (**1a**) with 20 mol% of NH_4I and 1 equiv. of oxone in water gave the corresponding product **3a** in moderate yield (Table 1, entry 1). When the reaction was performed in the absence of NH_4I, an extremely low yield of the desired product **3a** was observed along with unwanted 1-phenylethane-1,2-diol in quantitative yield, which is consistent with the report of Zhu and Ford,[14] and the reaction did not proceed in the absence of oxone (Table 1, entries 2 and 3). These reactions highlight the role of the iodine precursor and oxone in the present catalytic system for the synthesis of aldehydes from olefins. Surprisingly, the selectivity and reactivity of a reaction was greatly enhanced when the reaction was carried out in the presence of an amphiphilic surfactant, i.e., sodium dodecyl sulfate (SDS) (anionic) in water at room temperature (Table 1, entry 4). These preliminary findings suggest that the *in situ* generated hypoiodite species, i.e., $[OI]^-$ or (HOI) from NH_4I and oxone[15] in aqueous micellar media, could be suitable for our current investigation and encouraged us to further study the reaction for optimal conditions.

In an attempt to improve the yield of **3a**, various reaction parameters have been considered and examined sequentially. In this context, various other surfactants including cetyltrimethylammonium bromide (CTAB) (cationic), 3-(1-pyridino)-1-propanesulfonate (zwitterionic) and Tween® 80 (non-ionic) were investigated and we found that not one of the surfactants was appropriate to increase the yield of desired product above that obtained for SDS (Table 1, entries 5–7). Next, several oxidants were tested in the reaction and the replacement of oxone with $K_2S_2O_8$, *m*-CPBA, aq.H_2O_2 or aqueous TBHP furnished the product **3a** albeit in low or zero yield (Table 1, entries 8–11). Finally, the effects of solvent quantity and different mole ratios of reagents (NH_4I, oxone and SDS) on the reaction yield were established (Table 1, entries 12–18). After this extensive screening, we have

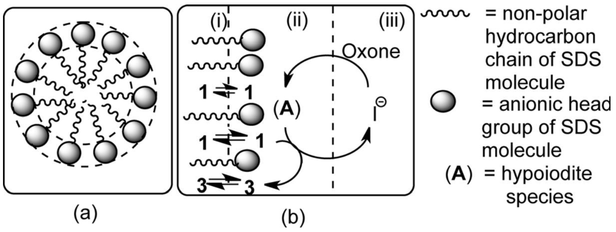


Figure 1. (a) A schematic representation of the nanometer micelle formed from SDS in water. (b) Illustration of different regions in aqueous micellar media: (i) interior of micelle (hydrophobic core); (ii) interfacial region (water-micelle interface); (iii) bulk aqueous media.

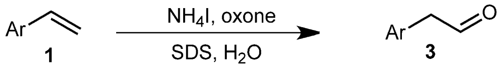
observed that the 20 mol%, 1 equiv. and 30 mol% of NH_4I, oxone and SDS, respectively, were optimum with respect to styrene to obtain the maximum yield of the desired product in water at room temperature (Table 1, entry 12).

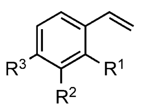
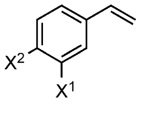
The higher reactivity and selectivity of a reaction in the presence of SDS molecules above their critical micelle concentration (CMC) in aqueous media might be attributed to the formation of nanometer micelles (Figure 1a). The *in situ* self-aggregation of SDS monomers in water was confirmed by DLS analysis and optical microscope studies, which indicated the formation of sphere-like shapes of the nanoreactors (see the Supporting Information).

Having the optimized conditions in hand, we investigated the versatility of this methodology with a wide variety of vinylarenes and the results are summarized in Table 2. Various electron-donating and electron-withdrawing groups were well tolerated with the present catalytic system and afforded the desired products **3a–3k** in good to excellent yields (Table 2, entries 1–11). The methyl-substituted styrenes **1b**, **1c** and **1d** reacted smoothly to give the corresponding aldehydes **3b**, **3c** and **3d** in 79–93% yields (Table 2, entries 2–4). The bulky alkyl group-substituted styrene **1e** exhibited slightly lower reactivity to generate the desired product **3e** in a synthetically useful yield of 55% after 6.33 h at room temperature, whereas the rate and yield of the reaction were enhanced when the temperature was raised to 55 °C (Table 2, entry 5). Notably, the fluorine-substituted styrenes were efficiently oxidized, irrespective of the position of substituent, to the respective aldehydes **3f** and **3g** in excellent yields (Table 2, entries 6 and 7). Meanwhile the chlorine and bromine substituents at the *para* position led to slightly higher yields than they do at a *meta* position of the phenyl ring of styrene (Table 2, entries 8–11). Unfortunately, the substrates 2-vinylnaphthalene and 4-vinylbiphenyl did not react under the present reaction conditions. This is possibly due to the poor solubility of these solid substrates in the present reaction medium.

To extend the scope of this reaction further, we investigated some 1,1-disubstituted, internal and aliphatic olefins and the results are summarized in Table 3. To our delight, the substrates **1l–1o** were well tolerated under the present reaction conditions and resulted in the formation of anti-Markovnikov products **3l–3o** in 83–95% yields (Table 3, entries 1–4). The α- and β-substituted styrene derivatives were oxidized to the corresponding products **3l**, **3m** and **3n** in 93%, 86% and 83% yields, respectively (Table 3, en-

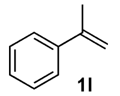
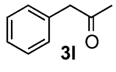
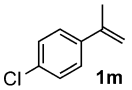
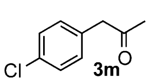
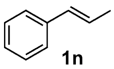
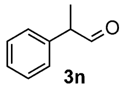
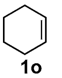
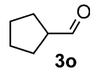
Table 2. Synthesis of aldehydes from vinyl arenes.[a,b]



Entry	Olefin **1**		Time [h]	Yield [%] of **3**
1[c]		$R^1 = R^2 = R^3 = H$; **1a**	0.13	93
2[c]		$R^1 = R^2 = H$, $R^3 = Me$; **1b**	0.45	93
3		$R^1 = R^3 = H$, $R^2 = Me$; **1c**	0.25	90
4[c]		$R^1 = R^3 = Me$, $R^2 = H$; **1d**	0.66	79
5		$R^1 = R^2 = H$, $R^3 = t$-Bu; **1e**	6.33 (0.75)[d]	55 (78)[d]
6[c]		$X^1 = H$, $X^2 = F$; **1f**	0.15	94
7[c]		$X^1 = F$, $X^2 = H$; **1g**	0.58	92
8[c,e]		$X^1 = H$, $X^2 = Cl$; **1h**	0.58	93
9[e]		$X^1 = Cl$, $X^2 = H$; **1i**	1.83	77
10[c,e]		$X^1 = H$, $X^2 = Br$; **1j**	2.91	92
11[c,e]		$X^1 = Br$, $X^2 = H$; **1k**	2.96	77

[a] *Reaction conditions:* substrate (1 mmol), NH_4I (20 mol%), SDS (30 mol%), oxone (1 mmol), H_2O (10 mL), room temperature.
[b] Isolated yields.
[c] Isolated as 2,4-DNP derivative **4**.
[d] Reaction at 55 °C.
[e] <2% of Markovnikov product was observed by ^1H NMR analysis of crude reaction mixture.

Table 3. Hypoiodite-catalyzed oxidation of 1,1-disubstituted, internal and aliphatic olefins.[a,b]

Entry	Olefin	Time [h]	Product	Yield [%]
1	 **1l**	1.16	 **3l**	93
2	 **1m**	7	 **3m**	86
3	 **1n**	1.25	 **3n**	83[c]
4	 **1o**	0.13	 **3o**	95[c]
5	1-dodecene	24	–	–

[a] *Reaction conditions:* substrate (1 mmol), NH_4I (20 mol%), SDS (30 mol%), oxone (1 mmol), H_2O (10 mL), room temperature.

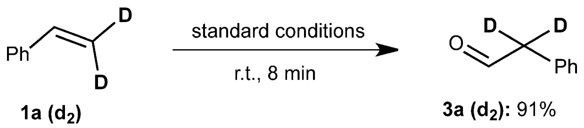
[b] Isolated yields.

[c] Isolated as 2,4-DNP derivative **4**.

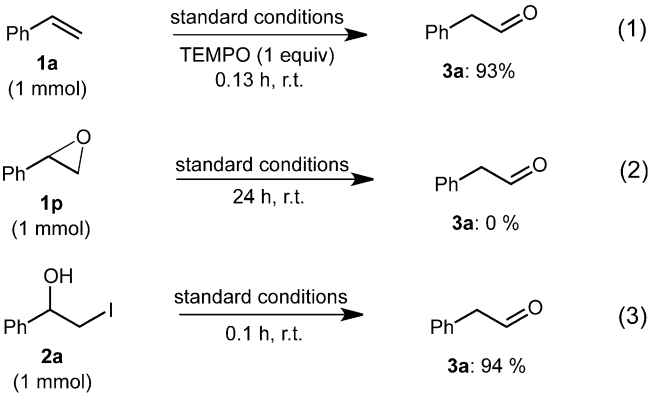
tries 1–3). Interestingly, the oxidation of cyclic olefin **1o** leads to the ring contraction product **3o** in 95% yield (Table 3, entry 4). However, the aliphatic acyclic alkene, i.e., 1-dodecene, under standard conditions did not yield the desired oxidation product and only the starting material was recovered after 24 h (Table 3, entry 5).

As can be seen from Table 2 and Table 3, it is evident that the vicinal migration of an aryl or alkyl moiety during the course of reaction leads to the desired anti-Markovnikov products. To confirm the migration process, we have investigated the reaction of β,β-dideuterated styrene under standard reaction conditions and obtained the corresponding aldehyde **3a (d$_2$)**, with two deuterium atoms at the benzylic position, in 91% yield (Scheme 2). This isotope labelling study unambiguously confirms the aryl or alkyl group migration in the oxidation of alkenes to the corresponding anti-Markovnikov products.

To explore the possible pathway for this novel catalytic reaction, several control experiments have been carried out and are illustrated in Scheme 3. When the styrene was subjected to our optimal conditions in the presence of TEMPO, the desired product **3a** was obtained without any change in the yield [Scheme 3, Eq. (1) and Table 2, entry 1]. This result clearly indicates that the styrene oxidation did not proceed through a radical mechanism. When 2-phenyloxirane (**1p)** was subjected to the standard reaction conditions, the formation of **3a** was not observed [Scheme 3, Eq. (2)], which indicates that **1p** may not be the intermediate[11a,b] in the aldehyde-selective oxidation process. Likewise, we examined the reaction of **2a** using the same procedure and obtained the product **3a** in 94% yield [Scheme 3, Eq. (3)]. This reaction suggests the co-iodo product **2a** as an intermediate in the regioselective oxidation of alkenes to aldehydes. To further confirm the intermediate in the reaction, we studied the styrene oxidation reaction under identical conditions at different time intervals and the yields[16] of products and unreacted styrene were plotted against time (see the Supporting Information). This reaction profile unequivocally reveals the intermediacy of iodofunctionalized product **2** in the oxidation of alkene **1** to corresponding anti-Markovnikov product **3**.

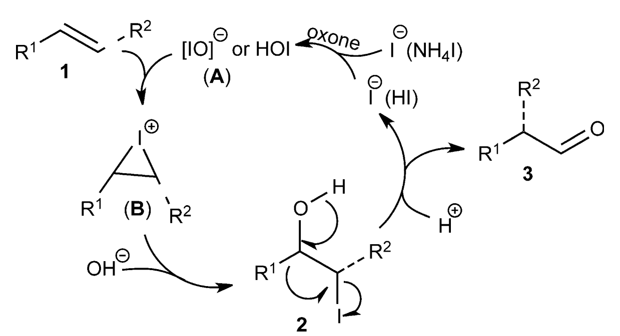


Scheme 2. Isotope labelling experiment.



Scheme 3. Control experiments.

Based on the observed results during the evolution of the scope of the reaction and control experiments, a plausible reaction mechanism for the formation of aldehydes from alkenes is depicted in Scheme 4. It is assumed that the oxone oxidizes I^- to HOI or $[IO]^-$ (**A**) in the aqueous phase and most of these oxidized iodine species reside in the immediate vicinity of an anionic micelle surface (Figure 1b).[17] The *in situ* generated hypoiodite species (**A**) reacts with the elec-



Scheme 4. Plausible mechanism for the hypoiodite-catalyzed oxidation of alkenes to aldehydes.

tron-rich double bond of alkene **1** [located at the interfacial region due to their equilibrium position between hydrophobic core and polar head group (Figure 1b)] to form a cyclic iodonium ion (**B**). Then, this three-membered cyclic iodonium ring is opened by the nucleophile (OH^-) to form a co-iodo intermediate **2**. De-iodination, in the presence of oxone, of intermediate **2** and subsequent 1,2-aryl/alkyl migration through a semipinacol rearrangement leads to the desired product **3**. Oxone converts the iodide ion generated in the first cycle into hypoiodite species (**A**) to further continue the catalytic cycle until complete consumption of the substrate.

In conclusion, we have developed a novel hypoiodite-catalyzed protocol for the anti-Markovnikov selective oxidation of alkenes under mild conditions. The present catalytic system utilizes stable, cheap and easy-to-handle inorganic salts as reagents (NH_4I as iodine pre-catalyst and oxone as terminal oxidant) and SDS as micelle forming surfactant in water. The nanoreactors formed by SDS in aqueous media were studied by optical microscopy and DLS. Moreover, the possible reaction pathway is also proposed through a tandem iodofunctionalization/1,2-aryl or alkyl migration based on preliminary mechanistic investigations.

Experimental Section

Materials and Methods

All chemicals (reagent grade) were purchased from Sigma–Aldrich and used as received without further purification. ^1H NMR spectra were recorded at 300 or 500 MHz and ^{13}C NMR spectra at 75 or 125 MHz in $CDCl_3$. The chemical shifts (δ) are reported in ppm units relative to TMS as an internal standard for ^1H 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), br s (broad singlet), d (doublet), dd (doublet of doublet), m (multiplet). GC analysis were carried out using GC Shimadzu (GC-2014) gas chromatograph equipped with FID detector and capillary column (EB-5, length 30 m, inner diameter 0.25 mm, film 0.25 μm). Mass spectra were recorded on a time of fight (TOF) mass spectrometer. Size and shape measurement studies were carried out using dynamic light scattering (DLS) and an optical microscope. TLC inspections were performed on Silica gel 60 F_{254} plates. Column chromatography was performed on silica gel (100–200 mesh) using *n*-hexane-EtOAc as eluent.

General Procedure

To a well stirred (for about 10 min) solution of SDS (30 mol%) in distilled water (10 mL) were added NH_4I (20 mol%) and alkene (1 mmol). The mixture was stirred for 30 min and then the oxone® (1 mmol) was slowly added. The reaction mixture was allowed to stir at room temperature until the alkene had completely disappeared (monitored by TLC, eluent: *n*-hexane-ethyl acetate or as indicated by the regeneration of iodine colour). The organic product mixture was extracted with DCM (3×25 mL). The organic layer was washed with 5% aqueous sodium thiosulfate solution (10 mL) and dried over anhydrous Na_2SO_4. The solvent was removed under vacuum and the residue was purified by column chromatography on silica gel using *n*-hexane-ethyl acetate as eluent to give desired products. The products **3a**, **3b**, **3d**, **3f–3h**, **3j–3k**, **3m** and **3o** were isolated as their corresponding 2,4-DNP derivatives **4a**, **4b**, **4d**, **4f–4h**, **4j–4k**, **4n** and **4o**, respectively. Spectroscopic data of all products (shown in Tables 2 and 3) and copies of their ^1H and ^{13}C NMR spectra are provided in the Supporting Information.

Acknowledgements

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References

[1] M. B. Gawande, V. D. B. Bonifácio, R. Luque, P. S. Branco, R. S. Varma, *Chem. Soc. Rev.* **2013**, *42*, 5522.

[2] a) J. H. Fendler, .E. J. Fendler, *Catalysis in Micellar and Macromolecular Systems*, Academic Press, New York, **1975**; b) G. S. Hartley, in: *Micellization, Solubilization and Microemulsions*, vol. 1, (Ed.: K. L. Mittal), Plenum Press, New York, **1977**; c) C.-H. Tung, L.-Z. Wu, L.-P. Zhang, B. Chen, *Acc. Chem. Res.* **2003**, *36*, 39; d) R. Nagarajan, E. Ruckenstein, *Langmuir* **1991**, *7*, 2934.

[3] For reviews, see: a) J. Zhang, X.-G. Meng, X.-C. Zeng, X.-Q. Yu, *Coord. Chem. Rev.* **2009**, *253*, 2166; b) G. Oehme, I. Grassert, E. Paetzold, R. Meisel, K. Drexler, H. Fuhrmann, *Coord. Chem. Rev.* **1999**, *185–186*, 585; c) T. Dwars, E. Paetzold, G. Oehme, *Angew. Chem.* **2005**, *117*, 7338; *Angew. Chem. Int. Ed.* **2005**, *44*, 7174; for selected recent examples, see: d) S. Handa, J. C. Fennewald, B. H. Lipshutz, *Angew. Chem. Int. Ed.* **2014**, *53*, 3432; e) M. Kunishima, K. Kikuchi, Y. Kawai, K. Hioki, *Angew. Chem.* **2012**, *124*, 2122; *Angew. Chem. Int. Ed.* **2012**, *51*, 2080; f) I. A. Fallis, P. C. Griffiths, T. Cosgrove, C. A. Dreiss, N. Govan, R. K. Heenan, I. Holden, R. L. Jenkins, S. J. Mitchell, S. Notman, J. A. Platts, J. Riches, T. Tatchell, *J. Am. Chem. Soc.* **2009**, *131*, 9746; g) G. Bianchini, A. Cavarzan, A. Scarso, G. Strukul, *Green Chem.* **2009**, *11*, 1517; h) J. Wu, F. Wang, Y. Ma, X. Cui, L. Cun, J. Zhu, J. Deng, B. Yu, *Chem. Commun.* **2006**, 1766; i) S. Roy, D. Das, A. Dasgupta, R. N. Mitra, P. K. Das, *Langmuir* **2005**, *21*, 10398; j) F. Wang, H. Liu, L. Cun, J. Zhu, J. Deng, Y. Jiang, *J. Org. Chem.* **2005**, *70*, 9424; k) S. Kobayashi, Y. Mori, S. Nagayama, K. Manabe, *Green Chem.* **1999**, *1*, 75.

[4] G. Dong, P. Teo, Z. K. Wickens, R. H. Grubbs, *Science* **2011**, *333*, 1609.

[5] a) C. Wang, A. Pettman, J. Basca, J. Xiao, *Angew. Chem.* **2010**, *122*, 7710; *Angew. Chem. Int. Ed.* **2010**, *49*, 7548; b) M. B. Smith, J. March, *March's Advanced Organic Chemistry*, 5th edn., Wiley, New York, **2001**; c) R. C. Larock, *Comprehensive Organic Transformations*, Wiley-VCH, Weinheim, **1999**.

[6] a) A. Chaintreau, D. Joulain, C. Marin, C.-O. Schmidt, M. Vey, *J. Agric. Food Chem.* **2003**, *51*, 6398; b) G. Mosciano, *Perfum. Flavor.* **1998**, *23*, 49.

[7] M. B. Smith, J. March, *March's Advanced Organic Chemistry*, John Wiley and Sons, New York, **2001**.

[8] a) M. Beller, J. Seayad, A. Tillack, H. Jiao, *Angew. Chem.* **2004**, *116*, 3448; *Angew. Chem. Int. Ed.* **2004**, *43*, 3368; b) J. Guo, P. Teo, *Dalton Trans.* **2014**, *43*, 6952.

[9] a) B. W. Michel, M. S. Sigman, *Aldrichimica Acta* **2011**, *44*, 55; b) R. Jira, *Angew. Chem.* **2009**, *121*, 9196; *Angew. Chem. Int. Ed.* **2009**, *48*, 9034; c) L. Hintermann, in: *Transition Metals for Organic Synthesis*, (Eds.: M. Beller, C. Bolm), Wiley-VCH, Weinheim, **2004**, p 279; d) J. Tsuji, *Palladium Reagents and Catalysts: New Perspectives for the 21st Century*, 2nd edn., Wiley, **2004**; e) J. M. Takacs, X.-T. Jiang, *Curr. Org. Chem.* **2003**, *7*, 369; f) J. Tsuji, H. Nagashima, H. Nemoto, *Org. Synth.* **1990**, *7*, 137; g) J. Tsuji, *Synthesis* **1984**, 369; h) J. Smidt, W. Hafner, R. Jira, R. Sieber, J. Sedlmeier, A. Sabel, *Angew. Chem.* **1962**, *74*, 93; *Angew. Chem. Int. Ed. Engl.* **1962**, *1*, 80; i) J. Smidt, W. Hafner, R. Jira, J. Sedlmeier, R. Sieber, R. Rüttinger, H. Kojer, *Angew. Chem.* **1959**, *71*, 176.

[10] anti-Markovnikov selective functionalization of alkenes was highlighted as a challenging task in catalysis two decades ago: J. Haggin, *Chem. Eng. News* **1993**, *71*, 23.

[11] a) J. Chen, C.-M. Che, *Angew. Chem.* **2004**, *116*, 5058; *Angew. Chem. Int. Ed.* **2004**, *43*, 4950; b) G.-Q. Chen, Z.-J. Xu, C.-Y. Zhou, C.-M. Che, *Chem. Commun.* **2011**, *47*, 10963; for a recent review, see ref.[8b]

[12] a) M. S. Yusubov, G. A. Zholobova, I. L. Filimonova, K.-W. Chi, *Russ. Chem. Bull. Int. Ed.* **2004**, *53*, 1735; b) M. S. Yusubov, G. A. Zholobova, *Russ. J. Org. Chem.* **2001**, *37*, 1179.

[13] For recent selected examples, see: a) X. Zhang, M. Wang, P. Li, L. Wang, *Chem. Commun.* **2014**, *50*, 8006; b) A. Yoshimura, C. Zhu, K. R. Middleton, A. D. Todora, B. J. Kastern, A. V. Maskaev, V. V. Zhdankin, *Chem. Commun.* **2013**, *49*, 4800; c) A. Yoshimura, K. R. Middleton, C. Zhu, V. N. Nemykin, V. V. Zhdankin, *Angew. Chem.* **2012**, *124*, 8183; *Angew. Chem. Int. Ed.* **2012**, *51*, 8059; d) M. Uyanik, D. Suzuki, T. Yasui, K. Ishihara, *Angew. Chem.* **2011**, *123*, 5443; *Angew. Chem. Int. Ed.* **2011**, *50*, 5331; e) M. Uyanik, H. Okamoto, T. Yasui, K. Ishihara, *Science* **2010**, *328*, 1376.

[14] W. Zhu, W. T. Ford, *J. Org. Chem.* **1991**, *56*, 7022.

[15] Oxone efficiently oxidizes halide ions (X^-) to electrophilic halogen species X^+ (HOX). For recent literature reports and reviews, see: a) ref.[13b]; b) K. V. V. Krishna Mohan, N. Narender, *Synthesis* **2012**, *44*, 15; c) H. Hussain, I. R. Green, I. Ahmed, *Chem. Rev.* **2013**, *113*, 3329.

[16] Yields based on GC analysis of crude sample after work-up.

[17] C. A. Bunton, F. Nome, F. H. Quina, L. S. Romsted, *Acc. Chem. Res.* **1991**, *24*, 357.

Hypoiodite-Catalyzed Regioselective Oxidation of Alkenes: An Expeditious Access to Aldehydes in Aqueous Micellar Media

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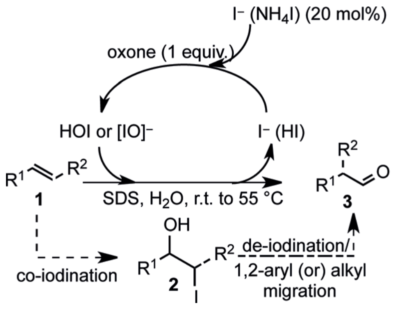
Macharla Arun Kumar, Kodumuri Srujana,
Chevella Durgaiah, Nama Narender*



- hypoiodite catalysis
- simple inorganic salts as reagents
- highly anti-Markovnikov selective
- mild conditions