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I_2-Catalyzed Regioselective Oxo- and Hydroxy-acyloxylation of Alkenes and Enol Ethers: A Facile Access to α-Acyloxyketones, Esters, and Diol Derivatives

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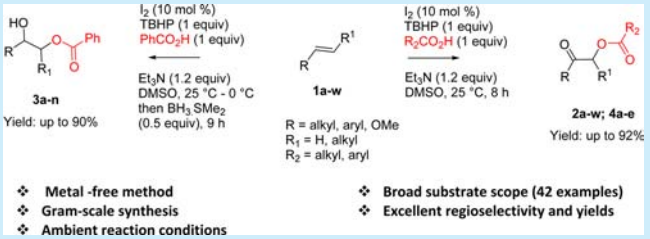
Supporting Information

ABSTRACT: I_2-catalyzed oxo-acyloxylation of alkenes and enol ethers with carboxylic acids providing for the high yield synthesis of α-acyloxyketones and esters is described. This unprecedented regioselective oxidative process employs TBHP and Et_3N in stoichiometric amounts under metal-free conditions in DMSO as solvent. Additionally, I_2-catalysis allows the direct hydroxy-acyloxylation of alkenes with the sequential addition of $BH_3{\cdot}SMe_2$ leading to monoprotected diol derivatives in excellent yields.



α-Acyloxyketones and esters are significant building blocks present in a variety of biologically interesting natural products, pharmaceuticals, and synthetic intermediates of broad utility.[1] In particular, mandelic acid derivatives have shown antioxidant,[2a] urinary antiseptic,[2b] anti-HIV,[2c] antitumor,[2d] antifungal,[2e] and antithrombic effects.[2f] Generally, these α-functionalized carbonyl derivatives are prepared either by the substitution of α-halo carbonyl compounds[3a]/insertion of α-diazoketones[3b] with alkaline carboxylates or the direct oxidative coupling of ketones with toxic heavy metal oxidants [e.g., $Pb(OAc)_4$, $Tl(OAc)_3$, $Mn(OAc)_3$, etc.][4] and Ru-catalyzed addition of carboxylic acids onto propargyl alcohols.[5] Further, α-acyloxylation of carbonyl compounds is reported using *N*-methyl-*O*-benzoylhydroxylamine[6] and benzoyl peroxide[7] as a carboxylic acid source. However, in the above reports, prefunctionalization of ketones/carboxylic acids is required prior to the α-acyloxylation step. Recently, direct oxidative coupling of ketones with carboxylic acids using a hypervalent iodine catalyst in the presence of an excess amount of $BF_3{\cdot}OEt_2$ in wet AcOH, *m*CPBA[8] or peracetic acid[9] as a co-oxidant has been reported to give α-acyloxyketones. Both intra- and intermolecular TBAI catalyzed oxidative coupling of carbonyl compounds with carboxylic acids/benzylic alcohols using either H_2O_2 or TBHP as a co-oxidant have been reported.[10,11] However, these protocols suffer from certain disadvantages such as use of a large excess of ketone motifs and co-oxidants, poor regioselectivity, and low yields. Moreover, the aforementioned methods are not suitable for α-acyloxylation of esters. Generally, α-acyloxy esters are prepared by the oxidation of alkyl trimethylsilylketene acetals with Pb(IV) carboxylates.[12a] In particular, mandelic acid derivatives are prepared by a metal-catalyzed intramolecular Cannizzaro reaction of α-ketoaldehydes[12b] or Friedel–Crafts reaction of aromatic compounds with glyoxylates.[12c]

The dihydroxylation of alkenes has been elegantly demonstrated with various transition metal catalysts[13] which are costly and toxic that led to the emergence of metal-free dihydroxylation of alkenes.[14] Again, the selective protection of one of the hydroxy groups in 1,2 diol is challenging and has been achieved using expensive reagents.[15] Recently, an $^nBu_4NI$-catalyzed direct and useful method for the synthesis of monoprotected diol from alkenes with TBHP as co-oxidant has been reported, although it is limited to styrenic substrates only.[16]

In recent times, I_2 catalysis, in combination with either aq. H_2O_2 or *tert*-butyl hydroperoxide as water-soluble co-oxidants, has been increasingly explored due to the environmentally benign and inexpensive oxidation reagents in place of rare or toxic heavy metal oxidants.[17]

To the best of our knowledge, use of catalytic electrophilic iodine in combination with stoichiometric co-oxidants from alkenes is not known. In 1998, Komatsu et al. reported iodine catalyzed aziridination of olefins using chloramine-T as the co-oxidant.[18] Herein, we report for the first time, a catalytic modification of the Woodward–Prevost oxidation for C–O bond formation using I_2/TBHP catalyzed oxo-acyloxylation of alkenes[19] and enol ethers with carboxylic acids in DMSO as solvent and Et_3N as base, giving α-acyloxyketones and esters (**2a–z**) in high yields and excellent regioselectivity (99%). In addition, one-pot "hydroxy-acyloxylation" has been described by sequential addition of $BH_3{\cdot}SMe_2$ in the reaction mixture that produces monoprotected diol derivatives (**3a–n**) in excellent yields (Scheme 1).

Initially, when styrene (1 mmol) was treated with a mixture containing benzoic acid (1 mmol), NBS (1 mmol), and Et_3N (1.2 mmol) at 25 °C in DMSO, the corresponding α-benzyloxyketone **2a** was obtained in 89% isolated yield with excellent regioselectivity (>99%) (Table 1). When a *stoichiometric* amount of I_2 was used as a halogen source, **2a** (90% yield) was indeed

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Scheme 1. I_2-Catalyzed Oxo- and Hydroxy-acyloxylation of Alkenes and Enol Ethers

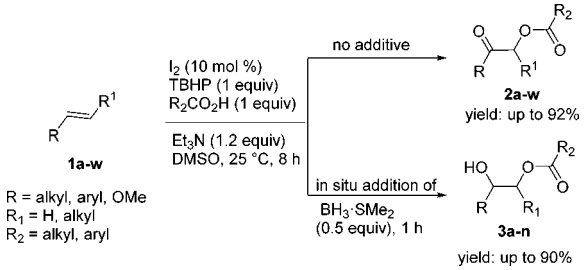
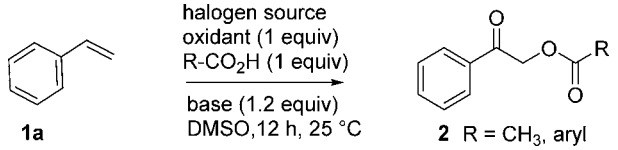


Table 1. I_2-Catalyzed Oxo-acyloxylation of Styrene with Carboxylic Acids: Optimization Studies[a]



no.	halogen (10 mol %)	oxidant (1 equiv)	base	R	yield of 2[b]
1	NBS[c]	–	Et_3N	Ph (**2a**)	89
2	I_2[c]	–	Et_3N	Ph	90
3	I_2	50% H_2O_2	Et_3N	Ph	13
4	I_2	$NaIO_4$	Et_3N	Ph	15
5	I_2	Oxone	Et_3N	Ph	8
6	NaI	TBHP	Et_3N	Ph	trace
7	$^nBu_4NI$	TBHP	Et_3N	Ph	11
8	I_2	TBHP	Et_3N	Ph	88 (53)[d] (89)[e]
9	I_2	TBHP	NaH	Ph	39
10	I_2	TBHP	KO^{t}Bu	Ph	72
11	I_2	TBHP	DBU	Ph	67
12	I_2	TBHP	K_2CO_3	Ph	47
13	I_2	TBHP	Et_3N	CH_3 (**4a**)	64
14	I_2	TBHP	Et_3N	4-NO_2-Ph (**4b**)	72
15	I_2	TBHP	Et_3N	4-Cl-Ph (**4c**)	76
16	I_2	TBHP	Et_3N	3-pyridyl (**4d**)	74
17	I_2	TBHP	Et_3N	1-propenyl (**4e**)	79

[a]Reaction conditions: styrene (1 mmol), carboxylic acid (1 mmol), halogen source (10 mol %), base (1.2 mmol), TBHP (5–6 M in decane) (1 mmol); in 8 mL of DMSO, 25 °C, 12 h. [b]Isolated yield after column chromatographic purification. [c]1 equiv of halogen source was used. [d]5 mol % of I_2 was used. [e]20 mol % of I_2 was used.

obtained with perfect regioselectivity. Encouraged by the result, it was of interest to develop a *catalytic* version of this useful oxo-acyloxylation process.

Thus, a series of experiments were conducted employing I_2 in catalytic amounts (10 mol %) along with other stoichiometric oxidants such as aq. H_2O_2, $NaIO_4$, Oxone, or TBHP, which gave **2a** in 13%, 15%, 8%, and 88% yields, respectively. With 5 mol % of I_2, a lowered yield of **2a** (53%) was however observed. Further modification in the iodine source, base, or solvent system (DMSO in combination with other solvents) did not show any significant improvement in the product yield. Other carboxylic acids (acetic, *p*-nitrobenzoic, *p*-chlorobenzoic, nicotinic, and crotonic acids) could be employed giving the corresponding oxo-acyloxylation products **4a**, **4b**, **4c**, **4d**, and **4e** in 64%, 72%, 76%, 74%, and 79% yields, respectively (Table 1).

The scope of the study was extended to substituted aromatics and alkenes, the results of which are subsequently displayed in Table 2. Several olefins with varied functional groups were found

Table 2. I_2-catalyzed Oxo- and Hydroxy-benzoyloxylation of Alkenes with Benzoic Acid: Substrate Scope[a]

		product yields (%)[b]	
no.	alkenes (**1a–n**)	**2a–n**	**3a–q**[c]
1	styrene (**1a**)	88	86
2	4-CH_3-styrene (**1b**)	85	84
3	4-Br-styrene (**1c**)	88	86
4	4-CN-styrene (**1d**)	82	79
5	4-OAc-styrene (**1e**)	84	83
6	3,4-$(OMe)_2$ styrene (**1f**)	83	81
7	PMBO-CH-CH=CH_2 (**1g**)	83	82[d]
8	allyl acetate (**1h**)	91	89
9	1-hexene (**1i**)	88	88
10	1-octene (**1j**)	92	90
11	1-decene (**1k**)	89	87
12	1-tridecene (**1l**)	86	84
13	cyclohexene (**1m**)	82	83 (3:1)[e]
14	indene (**1n**)	76	72 (3:1)[e]
15	stilbene (**1o**)	78[f]	–
16	Ph-CH=CH-CH_3 (**1p**)	81[f]	–
17	Ph-CH=CH-CH_2-OTBS (**1q**)	84[f]	–

[a]See footnote *a* under Table 1. [b]Isolated yields after column chromatographic purification. [c]*In situ* addition of anhydrous Na_2SO_4 and $BH_3{\cdot}SMe_2$ (0.5 equiv) to conditions in footnote *a* in Table 1. [d]Diol was obtained after excess of $BH_3{\cdot}SMe_2$ (2 equiv) was added. [e]*Anti*/*syn* ratio. [f]4-Nitrobenzoic acid was used instead of benzoic acid.

compatible in the reaction. Electron-neutral (4-CH_3), electron-deficient (4-CN), and electron-rich [3,4-$(OMe)_2$] groups on the aromatic nucleus were compatible and provided the corresponding products in excellent yields (82–85%, **2b**, **2d**, and **2f**).

Similarly, aliphatic olefins were found compatible under the optimal conditions and provided (**2g-n**) in good yields (82–92%). Moreover, disubstituted alkenes (**1m–1q**) underwent this oxo-acyloxylation smoothly providing the corresponding α-acyloxy ketones (**2m–2q**) in high yields with excellent regioselectivity (>99%, i.e. ketone group at the benzylic position).

We envisioned that addition of $BH_3{\cdot}SMe_2$ to the reaction mixture would enable us to obtain the corresponding diol derivatives **3a–q** (Table 2). To our delight, we indeed found that several styrenes and aliphatic alkenes underwent this "oxo-acyloxylation-reduction" process smoothly affording diol derivatives **3a–q** in 72–90% yields and excellent chemoselectivity (99%). Notably, use of excess of $BH_3{\cdot}SMe_2$ (2 equiv) to the reaction mixture afforded the corresponding diol in 82% yield (entry 7). Remarkably, internal alkenes gave the desired products in good diastereomeric ratio (3:1) with high yields (entry 13 and 14).Further, intramolecular version of hydroxy-acyloxylation was demonstrated in the macrolactonization of undec-10-enoic acid (**1r**), which gave 12 membered hydroxy lactone **3r** in 82% yield (Scheme 2).[19]

Table 3 summarizes the application of the optimized reaction conditions to a range of enol ethers in an effort to expand the scope of this oxo-acyloxylation reaction. Enol ethers with *p*-substituted electron-rich or -poor groups and furan substitutions proved to be good substrates for this transformation, affording

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Scheme 2. I_2-Catalyzed Hydroxy-lactonization of Undec-10-enoic Acid

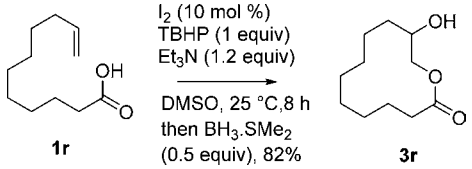
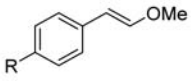
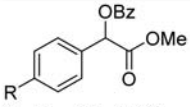
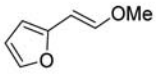
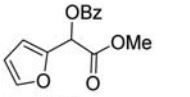
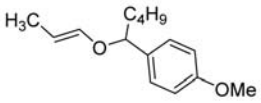
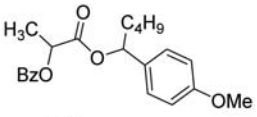
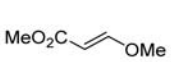
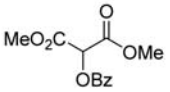
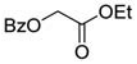
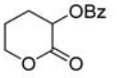


Table 3. I_2-Catalyzed Oxo-benzoyloxylation of Enol Ethers with Benzoic Acid: Substrate Scope[a]

substrates	products with yields
	
1s : R = Br **1t** : R = CN **1u** : R = NO_2	**2s** : R = Br : 78% **2t** : R = CN : 81% **2u** : R = NO_2: 82%
	
1v	**2v** : 78%
	
1w	**2w** : 74%
	
1x	**2x** : 83 %
	
1y	**2y** : 89%
	
1z	**2z** : 84%

[a]For reaction conditions, see footnote *a* under Table 1: Bz = benzoyl.

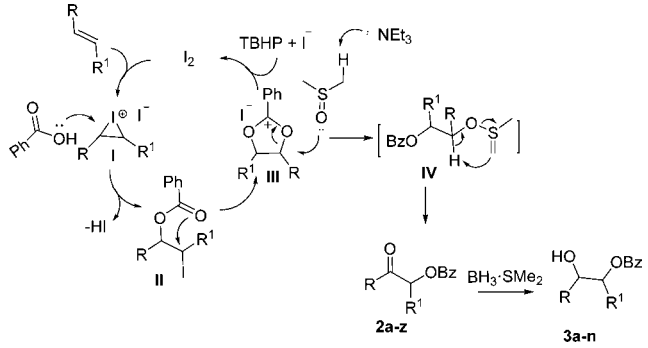
the corresponding mandelic and lactic acid derivatives **2s–v** in high isolated yields (74–82%).

Aliphatic enol ethers (**1w–y**) also gave the desired products **2w–y** in high yields. In addition, when cyclic enol ether **1z** was used, the desired product **2z** was obtained in 84% yield.

To gain some insight into the mechanism of the reaction, the following experiments were performed: (i) no reaction was observed in the absence of either benzoic acid or Et_3N; (ii) in the case of styrene, the iodo compound **II** was isolated (20% yield after 2 h) and characterized completely (GC-MS, ^1H and ^{13}C NMR) which eliminates the role of hypervalent iodine in the mechanism ; (iii) further treatment of **II** with DMSO and Et_3N afforded the desired product **2a** in 62% yield; (iv) Table 1 (entries 2 and 8) suggests that TBHP can be used as a co-oxidant.

According to the aforementioned information and based on previous reports, a proposed mechanism for this I_2-catalyzed oxidative functionalization of alkenes is outlined in Scheme 3. Initially, the substrate alkene reacts with I_2 to afford the iodonium ion intermediate **I**, which undergoes regioselective ring opening

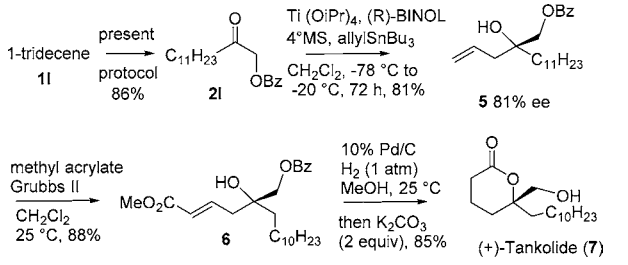
Scheme 3. Probable Catalytic Cycle for Oxo- and Hydroxy-acyloxylation of Alkenes



with benzoic acid giving the iodo compound **II**. The proposed key intermediate species **III**,[14c] formed from **II** by the anchimeric assistance shown by the benzoate group, reacts with DMSO in a regioselective manner to give hydroxy ylide **IV** with the liberation of an iodide ion. The iodide ion is then reoxidized with TBHP to regenerate I_2 while elimination ($-Me_2S$) from **IV** could then be undertaken to provide the desired products **2a–z**, which on borane reduction gave diol derivatives **3a–n**.

Its application is illustrated in the total synthesis of (+)-Tanikolide **7**,[20] a brine-shrimp toxin and antifungal marine metabolite. Thus, α-benzoyloxyketone **2l**, obtained from 1-tridecene by the present protocol, was subjected to asymmetric Keck allylation to give homoallylic alcohol **5** (81% yield; 81% ee). Compound **5** was then subjected to cross-metathesis with methyl acrylate using Grubbs' second generation catalyst to give unsaturated ester **6** in 88% yields, which was finally reduced and hydrolyzed to afford (+)-Tanikolide in 85% yield (Scheme 4).

Scheme 4. Synthesis of (+)-Tanikolide



In summary, we have demonstrated that the oxo- and hydroxy-acyloxylation process of alkenes and enol ethers with carboxylic acids can be achieved using metal-free catalytic systems. This operationally simple and efficient method provides a new approach toward the synthesis of α-acyloxyketones, esters (**2a–z**), and diol derivatives (**3a–n**) with a broad substrate scope. We believe that the macrolactonization directly from unactivated carboxylic acid would serve as a competent method and find tremendous applications in the synthesis of widely occurring macrolides. More importantly, this inexpensive catalyst/oxidant system provides for a single-step, metal-free dihydroxylation process directly from alkenes, thereby complimenting OsO_4 catalyzed dihydroxylation of alkenes.

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■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures, product characterization, copies of NMR spectra for **2a−z**, **3a−n**, **4−7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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