Organic & Biomolecular Chemistry

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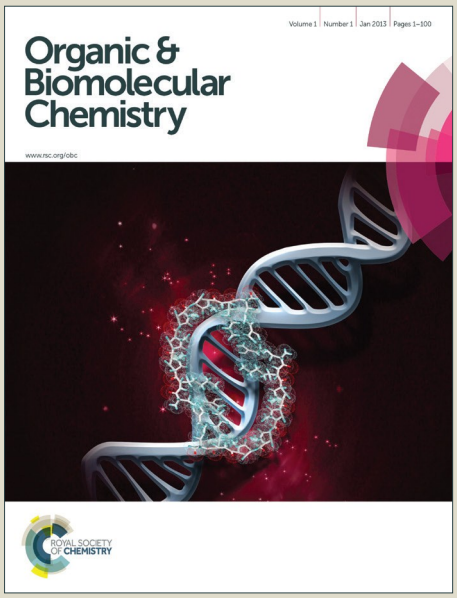

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DOI: 10.1039/C5OB01929J

Journal Name

ARTICLE

A chemoselective α-aminoxylation of aryl ketones: A cross dehydrogenative coupling reaction catalysed by Bu_4NI

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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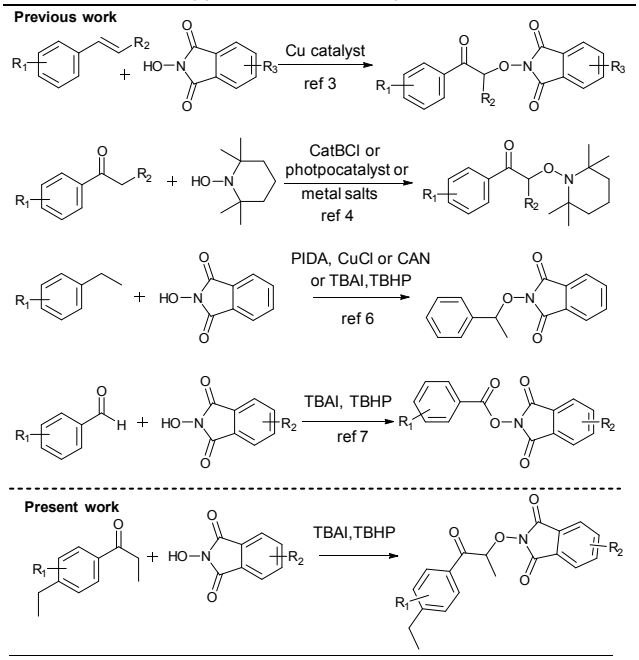
Tetrabutyl ammonium idodide (TBAI) catalyzed α-aminoxylation of ketones using aq TBHP as oxidant has been accomplished. We have shown that the CDC (cross dehydrogenative coupling) reactions of ketones with *N*-hydroxyimidates such as *N*-hydroxysuccinimide (NHSI), N-hydroxyphthilimde (NHPI), *N*-hydroxybenzotriazole (HOBT) and 1-hydroxy-7-azabenzotriazole (HOAT) lead to corresponding oxygenated products in good to moderate yields. The application of this method has been demonstrated by transforming a few coupled products into synthetically useful intermediates and products.

Introduction

C-H Functionalization strategy is a rapidly expanding area in organic synthesis as it offers high impetus for developing novel, short and useful methodologies for synthesizing a variety of organic compounds.[1] α-Aminoxylation of ketones using NHPI (N-hydroxyphthalimide) derivatives through C-H bond functionalization strategy is attractive as it leads to the formation of α-aminoxylation products. As radical reactions are known to play a vital role in redox chemistry of biological systems, similar approaches have gained significant momentum in designing novel oxidative reactions. The radical sources such as NHPI and its derivatives are well known oxidants for the oxidation of benzylic, and allylic hydrocarbons.[2] Recently, Punniyamurthy,[3a] Woerpel[3b] and Liang[3c] independently reported copper catalysed α-aminoxylation of alkenes by employing NHPI. Similarly TEMPO, and nitroso derivatives are also used as precursors for α-aminoxylation of ketones.[4,5] Studer's group reported α-aminoxylation of ketones using TEMPO and chlorocatecholborane.[4a] Recently Jiao's group reported α-aminoxylation of active methylene compounds using TEMPO and cerium ammonium nitrate.[4b] Chang and co-workers reported a Cu catalyzed functionalization of benylic and allylic C-H bonds using NHPI and hypervalent iodine reagents,[6a] where as Terent'ev and co-workers reported a cerium(IV) ammonium nitrate catalyzed functionalization of benylic and allylic C-H bonds using NHPI.[6b] Barbas and group has developed a CDC reactions of aldehydes with N-hydroxyimides (Scheme 1).[7] The oxidative functionalization of carbonyl compounds at α-position using hypervalent iodine compounds is gaining lot of momentum.[8] In this regard, our interest was to design metal-free, catalytic CDC reactions to synthesize useful intermediates that can be transformed to a variety of functional groups.[9] Herein we report a CDC reaction at the α-position of ketones using NHPI, NHSI, HOBT and HOAT as coupling partners for the formation of C-O bonds using catalytic amount of TBAI and aq TBHP as an oxidant. The salient features of the present method is that (i) it is performed under metal-free conditions, (ii) provides an extensive, wide range of substrate scope and (iii) utility of environmentally friendly reagents such as TBAI (catalytic amount) and aq TBHP that generates *tert*-butanol as by-product.

Scheme 1. Various approach for α-aminoxylation



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† Electronic Supplementary Information (ESI) available: For experimental procedures, spectral data and spectra. See DOI: 10.1039/x0xx00000x

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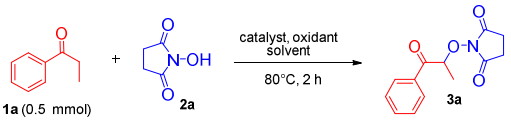
DOI: 10.1039/C5OB01929J

Results and Discussion

Initial screening studies were carried out using propiophenone (**1a**) and *N*-hydroxysuccinimide (**2a,** NHSI) as model substrates. The solvent screening studies indicated that the solvents such as CH_3CN, DCE, ethyl acetate and toluene, are not suited for the reaction (entry 1, Table 1, also see the Electronic Supplementary Information). Further, solvent screening studies revealed that DMA is the most suitable solvent which resulted in the formation of the product **3a** in 64% yield (entry 2, Table 1), whereas other solvents such as DMSO, DMF furnished product **3a** in low yields (54 and 60%, respectively, entries 3-4). Catalyst screening studies revealed that TBAI is the most suitable catalyst while KI or NaI furnished the product **3a** in 63, and 60% respectively (entries 5-6). Further, NIS, molecular iodine or TBAB found not suitable as the reactiond of **1a** with these catalysts did not furnish the product **3a** (entries 7-9, Table 1). Employing TBHP in decane (5.5M) as an oxidant furnished **3a** in 60% yield (entry 10, Table 1), whereas the reaction did not proceed with other oxidants such as aq H_2O_2, cumene hydroperoxide, dibenzoylperoxide, ditertiarybutylperoxide, *m*-CPBA, or $K_2S_2O_8$ (entry 11, Table 1, also see the Electronic Supplementary Information). Decreasing or increasing the amount of NHSI (**2a**), propiophenone (**1a**), TBAI or TBHP did not improve the yield of **3a** (entries 12-17, Table 1). This observation clearly indicates that propiophenone is decompositing under the reactionconditions. Addition of *p*-TSA as an acid additive was detrimental to the reaction, while the addition of piperidine as additive decreased the yield to 55% (entries 18-19). With these screening studies, further exploration for studuying the scope of the reaction was carried out using ketone (1 equiv), NHSI (**2a**, 3 equiv), TBAI (10 mol%), TBHP (1 equiv) in DMA at 80 °C.

Having found the optimal reaction conditions, the scope of the coupling reaction was explored using a variety of aryl ketones with *N*-hydroxysuccinimide (**2a**). The reaction was facile with ketones such 1-phenylbutan-1-one, 1-phenylpentan-1-one, 6-methyl-1-phenylheptan-1-one and 1-phenyldecan-1-one to furnish the coupled products **3b, 3c, 3d,** and **3e** in good yields (63, 66, 60, and 61%, respectively, Table 2). Further, it was found that the reaction of NHSI (**2b**) with ketones derivatives that contain free benzylic positions such as 1-(4-ethylphenyl)propan-1-one, 1-(4-decylphenyl)propan-1-one, 1,3-diphenylpropan-1-one, 3-(naphthalen-1-yl)-1-

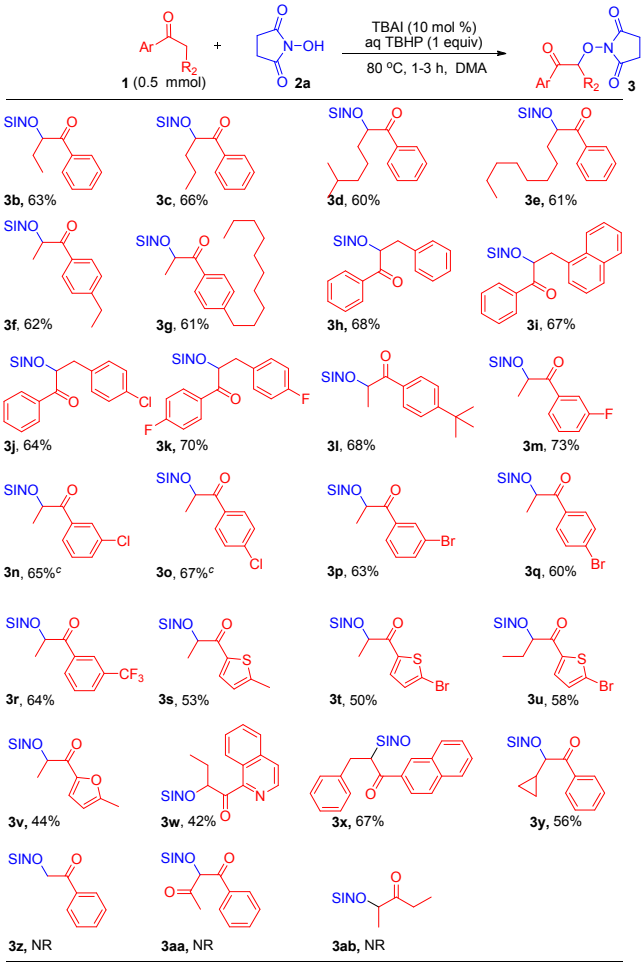
Table 1. Optimization studies[a]



Entry	Catalyst (mol%)	Oxidant (1 equiv)	Solvent	Conversion[b]
1	TBAI (10)	aq.TBHP	solvents	NR
2	**TBAI (10)**	**aq.TBHP**	**DMA**	**64%**
3	TBAI (10)	aq.TBHP	DMSO	54%
4	TBAI (10)	aq.TBHP	DMF	60%
5	KI (10)	aq.TBHP	DMA	63%
6	NaI (10)	aq.TBHP	DMA	60%
7	I_2 (10)	aq.TBHP	DMA	NR
8	NIS (10)	aq.TBHP	DMA	NR
9	TBAB (10)	aq.TBHP	DMA	NR
10	TBAI (10)	TBHP in decane	DMA	60%
11	TBAI (10)	oxidants	DMA	NR
12[c]	TBAI (10)	aq.TBHP	DMA	64%
13[d]	TBAI (10)	aq.TBHP	DMA	50%
14[e]	TBAI (10)	aq.TBHP	DMA	34%
15	TBAI (5)	aq.TBHP	DMA	55%
16	TBAI (15)	aq.TBHP	DMA	64%
17[f]	TBAI (10)	aq.TBHP	DMA	50%
18[g]	TBAI (10)	aq.TBHP	DMA	NR
19[h]	TBAI (10)	aq.TBHP	DMA	55%
20	-	aq.TBHP	DMA	NR

[a]Reaction conditions: **1a** (0. 5 mmol), **2a** (1.5 mmol), solvent (1 mL), oxidant (0.5 mmol), catalyst (0.05 mmol) in 1ml of DMA at 80 °C. [b]Isolated yield. [c]4 Equiv of **2a**. [d]2 Equiv of **2a**.[e]3 Equiv of **1a** and 1 equiv of **2a**.[f]2 Equiv of aq TBHP. [g]20 mol % PTSA used. [h]10 mol % piperidine used. DMA (*N,N*-dimethyl acetamide). NR=No reaction.

Table 2. Coupling of NHSI[a,b]



[a]Reaction conditions: **1a** (0.5 mmol), **2a** (1.5 mmol), solvent (1 mL), aq TBHP 70% (0.5mmol), TBAI (0.05 mmol) in 1mL of DMA at 80 °C. [b]Isolated yield. [c]The reaction was performed using 1g of ketone. NR= No recation.

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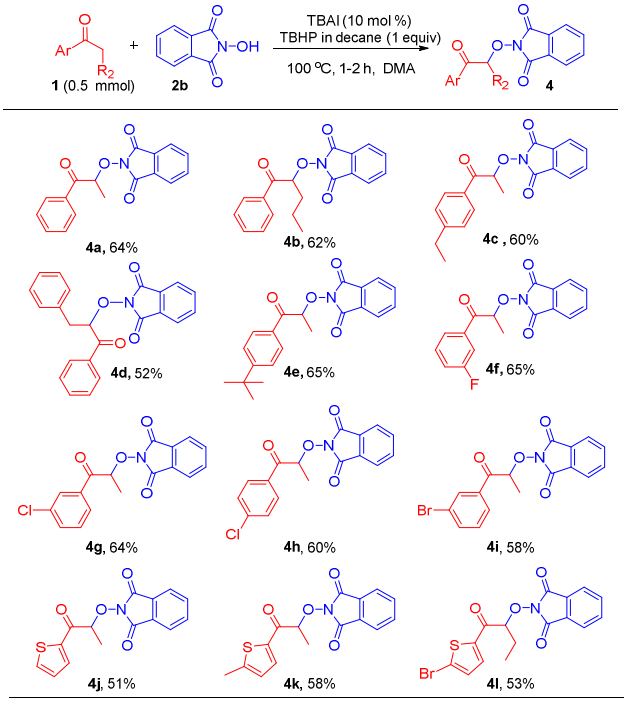
phenylpropan-1-one, 3-(4-chlorophenyl)-1- phenylpropan-1-one, and 1,3- bis(4-fluorophenyl)propan-1-one resulted in the formation of coupled products **3f, 3g, 3h, 3i**, **3j,** and **3k** in good yields (62, 61, 68, 67, 64, and 70%, respectively, Table 2). These reactions are selective in which benzylic positions are intact while the reaction occurs only at α-position to ketone. 1-(4-(*tert*-Butyl)phenyl)propan-1-one furnished product **3l** in 68% yield (Table 2). The scope of this reaction was studied with a variety of halogenated aryl ketones such as 1-(3-fluorophenyl)propan-1-one, 1-(3- chlorophenyl)propan-1-one, 1-(4-chlorophenyl)propan-1-one, 1-(3-bromophenyl)propan-1-one, 1-(4-bromophenyl)propan-1-one, and 1-(4-(trifluoromethyl)phenyl)propan-1-one, whcih furnished their corresponding coupled products **3m, 3n, 3o, 3p, 3q,** and **3r** in good yields (73, 65, 67, 63, 60, and 64%, respectively, Table 2). The coupling reaction with thiophene derivatives such as 1-(5-methylthiophen-2-yl)propan-1-one, 1-(5-bromothiophen-2-yl)propan-1-one and 1-(5-bromothiophen-2-yl)butan-1-one to afforded the coupled products **3s, 3t,** and **3u** in moderate yields (53, 50, and 58%, respectively, Table 2). Similarly ketones such as 1-(5-methylfuran-2-yl)propan-1-one, 1-(isoquinolin-1-yl)butan-1-one, 1-(naphthalen-2-yl)-3-phenylpropan-1-one, and 2-cyclopropyl-1-phenylethan-1-one furnished the coupled products **3v**, **3w, 3x** and **3y** in moderate yields (44, 42, 67, and 56%, respectively, Table 2). The coupling reaction of NHSI with ketones such as acetophenone, 1-phenylbutane-1,3-dione, and pentan-3-one was not successful.

After completing the coupling of NHSI, we continued the exploration of the reaction with *N*-hydroxyphthilimde (**2b**, NHPI), which is one of the derivatives of **2a**. Coupling of NHPI with ketones would provide new molecules which are useful intermediates in organic synthesis.[3] Under the optimal reaction condition that was employed for coupling of ketone **1a** with NHSI using aq TBHP (70%) as an oxidant resulted in the formation of the coupling product along with phthalic acid as an inseparable mixture. This problem was circumvented by using TBHP in decane (5.5M) as an oxidant. Hence, the coupling reaction of NHPI (**2b**) with ketones was carried out using TBAI (10 mol %) and TBHP (in dacane) as an oxidant. Thus, NHPI (**2b**) underwent a smooth coupling reaction with propiophenone, 1-phenylpentan-1-one, to afford the corresponding C-O coupled products **4a**, and **4b** in good yields (64, and 62%, respectively, Table 3). Benzylic and allylic hydrocarbons are known to undergoes oxidation with NHPI (**2b**) to form alcohols, ketones, or carboxylic acids.[2] The combination of TBHP and TBAI is known to activate benzylic as well as allylic positions.[11] Apart form this, *N*-hydroxyphthalimide (NHPI) is a well known reagent to couple at benzylic or allylic positions.[6] Interestingly, in the reaction of ketones such as 1-(4-ethylphenyl)propan-1-one,and 1,3-diphenylpropan-1-one, which have free benzylic position, with NHPI (**2b**) furnished the coupled products **4c** and **4d** in good to moderate yields (60, and 52%,respectively, Table 3). It is note worthy that these reactions exhibited a remarkable chemoselctivity in coupling NHPI at the α-position to ketone, while the benzylic position was intact. 1-(4-(*tert*-Butyl)phenyl)propan-1-one also furnished the NHPI coupled product **4e** in 65% yield (Table 3). Similarly, halogen substituted propiophenone derivatives such as 1-(3-fluorophenyl)propan-1-one, 1-(3-chlorophenyl)propan-1-one, 1-(4-chlorophenyl)propan-1-one, and 1-(4-bromophenyl)propan-1-one underwent a smooth reaction with NHPI (**2b**) to furnish the coupled products, **4f**, **4g, 4h,** and **4i** in good yields (65, 64, 60, and 58%, respectively, Table 3). Thiophene containing ketone derivatives such as 1(thiophene-2-yl) propan-1-one, 1-(5-methylthiophen-2-yl)propan-1-one and 1-(5-bromothiophen-2-yl)butan-1-one derivatives underwent a facile coupling with NHPI **(2b)** to furnish the product **4j, 4k,** and **4l** in moderate yields (51, 58, and 53%, respectively, Table 3).

Table 3. Coupling of NHPI[a,b]



[a]Reaction conditions: **1a** (0.5 mmol), **2a** (1.5 mmol), solvent (1 mL),TBHP in decane 5.5M (0.5 mmol), TBAI (0.05 mmol) in 1mL of DMA at 100 °C. [b]Isolated yield.

The versatile coupling reaction of NHSI (**2a**) and NHPI (**2b**) with variety of ketones led us to undertake the coupling reactions of *N*-hydroxybenzotriazole (HOBt, **2c**) and 1-hydroxy-7-azabenzotriazole (HOAT, **2d**) hoping that the free N-OH groups of HOBT and HOAT could couple at *α*-position of ketones. Therefore, the coupling reactions of HOBt (**2c**) and HOAT (**2d**) were studied using propiophenone derivatives under standard reaction conditions with aq TBHP using DMA as a solvent. This reaction resulted in the formation of benzoic acid as the major product. This problem was circumvented by performing the reaction using DMSO as the solvent, which furnished corresponding HOBt (**2c**) and (HOAT) (**2d**) coupled products in moderate yields. Thus, HOBt (**2c**) underwent a smooth coupling reaction with propiophenone to afford **5a** in moderate yield (42%). Similarly, halogen substituted

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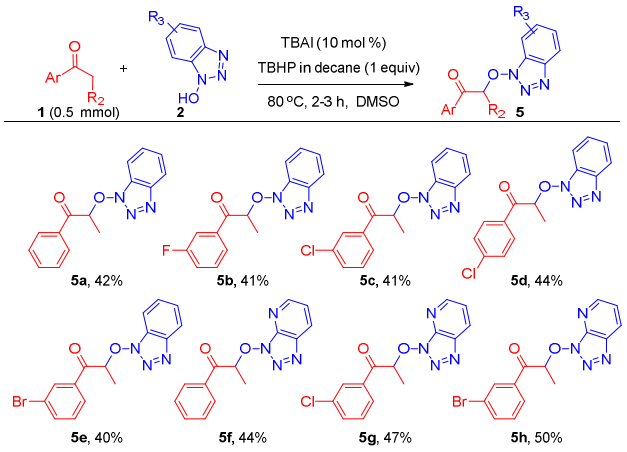
propiophenone derivatives such as 1-(3-fluorophenyl)propan-1- one, 1-(3-chlorophenyl)propan-1-one, 1-(4-chlorophenyl)propan-1-one and 1-(3-bromophenyl)propan-1-one underwent a smooth reaction with HOBt (**2c**) to furnish the coupled products **5b, 5c, 5d** and **5e** in moderate yields (41, 41, 44, and 40%, respectively, Table 4). Scope of the coupling reaction of 1-hydroxy-7-azabenzotriazole (HOAT, **2d**) was extended for the coupling reaction of propiophenone, 1-(3-chlorophenyl)propan-1-one and 1-(3-bromophenyl)propan-1-one which afforded corresponding HOAT coupled products **5f**, **5g** and **5h** in moderate yields (44, 47, and 50%, respectively, Table 4).

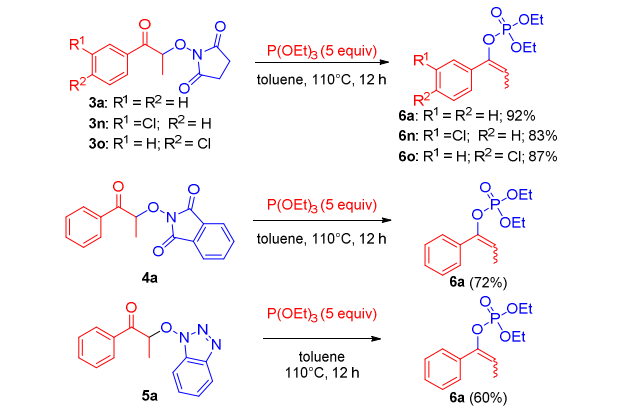
Table 4. Coupling of HOBT and HOAT[a,b]



[a]Reaction conditions: 1a (0.5 mmol), **2c** or **2d** (1.5 mmol), solvent (1 mL), TBHP in decane 5.5M (0.5 mmol), TBAI (0.05 mmol) in 1mL of DMSO at 80°C. [b]Isolated yield.

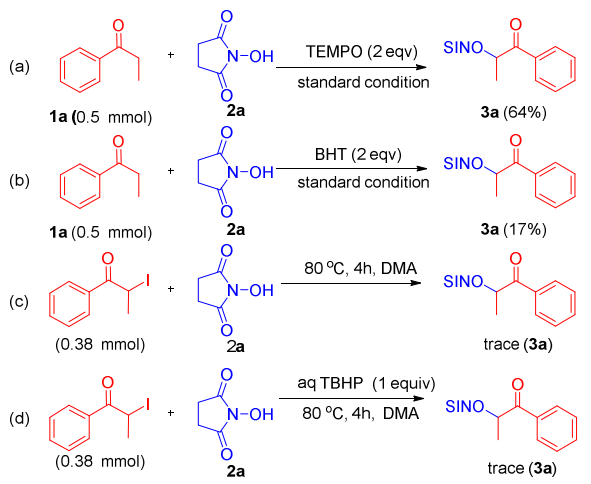
The application of the α-oxygenation has been demonstrated by transforming coupled products into synthetically useful intermediates and products. The vinyl phopshates are well known precursors for several cross-coupling reactions.[10] As can be seen in Scheme 2, the succinimide coupled products (**3a**, **3n**, and **3o**), were subjected for a reaction with $P(OEt)_3$ under reflux conditions to obtain the corresponding vinyl phosphates such as **6a**, **6n**, and **6o** in good yields (92, 83, and 87%, respectively, Scheme 5). Similarly, phthalimide coupled product (**4a**) in a reaction with $P(OEt)_3$ under reflux conditions furnished the corresponding vinyl phosphates such as **6a** in good yield (72%, Scheme 2). To demonstrate the utility of HOBT coupled product, **5a** has been subjected for a reaction with $P(OEt)_3$ under reflux conditions to get vinyl phosphate **6a** (60%, Scheme 5).

Scheme 2. Synthetic applications



To understand the mechanism of this reaction, a few control experiments were performed. First, the reaction of propiophenone (**1a**) with NHSI (**2a**) under the standard reaction conditions in the presence of TEMPO was found proceed well to form the corresponding **3a** in 64% (Scheme 3) indicated that PINO radical is more reactive than TEMPO radical under the reaction condition, where as with BHT (2eqv) under standard conditions furnished **3a** in 17% yield, indicating that the reaction proceeding through a radical mechanism. Further to find whether the 2-iodo-1-phenylpropan-1-one is an intermediate in the above reaction, two independent experiments were performed. As can be seen, the reaction of 2-iodo-1-phenylpropan-1-one in the presence or in the absence of TBHP did not furnish the expected product **3a** ((c) and (d) Scheme 3).

Scheme 3. Control experiments for mechanistic studies



Based on these experiments and the literature precedence,[8a, 8b, 9f, 11] we believe that I^- reacts with TBHP to form $[Bu_4N]^+[IO]^-$ (**I**) and which further reacts with excess TBHP to form $[Bu_4N]^+[IO_2]^-$ (**II**).[8a, 8b, 9f, 11] The species **II** thus generated undergoes an electrophilic addition with propiophenone to generate dihypoiodate species **III**, which form a radical which is combine with PINO to form **3a.** Alternatively which upon nucleophlic displacement by species **III** furnishes **3a** (Scheme 4).

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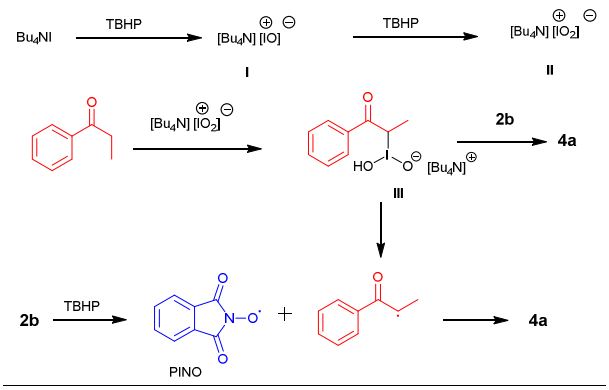
Scheme 4. A tentative mechanism



Conclusions

In summary, we have uncovered a Bu_4NI-catalyzed chemoselective oxygenation of ketones to obtain a high α-selectivity using TBHP as an oxidant. Reaction is chemoselective, aryl methyl ketones, aliphatic ketones as well as benzyllic position are inactive under the reaction condition. The versatility of the reaction has been established by coupling *N*-hydroxysuccinimide (NHSI), N-hydroxyphthilimde (NHPI), N-hydroxybenzotriazole (HOBT) and 1-hydroxy-7-azabenzotriazole (HOAT) to a variety of ketones. The application of teh reaction has been demonstrated by synthesizing synthetically useful intermediates and products vinyl phosphates as well as α-haloketone.

Acknowledgements

The authors thank IISc, SERB (NO.SB/S1/OC-56/2013), New-Delhi,and RL Fine Chem for financial support and Dr. A. R. Ramesha (RL Fine Chem) for useful discussion. YS thanks CSIR for a fellowship.

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