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Metal Free One-Pot Synthesis of α-Ketoamides from Terminal Alkenes

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A practical approach towards the synthesis of α-ketoamides from readily available terminal alkenes (styrenes) has been developed. Use of inexpensive I_2/2-iodoxybenzoic acid (IBX) in dimethyl sulphoxide (DMSO) as oxidant under the metal free one-pot condition makes this methodology versatile.

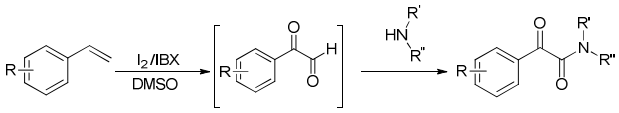
Introduction

α-Ketoamides are important functional group in a wide range of pharmaceuticals, drugs and natural products. α-Ketoamide based compounds have also been reported to act as anticancer agents, HIV inhibitor, FIV protease inhibitors and histone deacetylase inhibitors.[1-6] The activities of transition state inhibitory immunosuppressive drugs like tacrolimus and sirolimus can be attributed to the presence of this moiety.[7] Apart from this biologically important application, they act as valuable precursors and synthetic intermediates in many functional group transformations.[8,9]

Due to the importance of the α-ketoamide scaffold, several synthetic methodologies have been developed. To overcome the disadvantages associated with the classical method of synthesizing α-ketoamides from α-ketoacids by amidation with activating agents,[10] metal catalyzed methodologies came into the picture. In the metal based methodologies, Pd and Cu take an unique place in the synthesis of tertiary α-ketoamides and some of their representative approaches are palladium-catalyzed double carbonylation of aryl halides and amines using carbon monoxide,[11] copper-catalyzed aerobic oxidative coupling of aryl acetaldehydes,[12] copper-catalyzed aerobic oxidative cross-dehydrogenative coupling of amine and α-oxoaldehyde,[13] copper-catalyzed direct oxidative synthesis of α-ketoamides from aryl methyl ketones etc.[14,15] However, the drawbacks associated with the use of transistion metals which are invovled, hazardous nature and sensitivity towards moisture and air favoured the development of metal free methodologies. Also avoiding the metals as catalyst in reaction is one of the best choices for pharmaceutical industry to keep the chances of metal contamination at bay.

Most appealing approaches in the recent time mainly uses carbonyl based starting materials such as aryl methyl ketones and oxoaldehydes under oxidative amidation condition with oxidants like *tert*-butyl hydrogen peroxide (TBHP) and selenium dioxide.[16-19] Aryl methyl alcohols, amides and β-diketones have also been used as the starting materials for the synthesis of α-ketoamides.[20,21] On the other hand formamides generally used as the source of the amine moiety, but less availability of formamides limit the practical applicability of the methodologies.

Very recently, Deshidi *et al.* reported I_2 mediated α-ketoamide from terminal alkenes. In addition, they also reported the synthesis of α-ketoamide using I_2/TBHP under solvent free conditions.[22] As part of our ongoing research towards developing metal free organic transformation,[23] we here in report the one-pot synthesis of α-ketoamide from styrenes (Scheme 1). The idea behind in this method to make the use of 2-oxoaldehyde intermediate formed *in situ* from styrene in presence of IBX in DMSO, for coupling with amines to give hemiaminal type intermediate which then is expected to get further oxidized by IBX to give the desired α-ketoamides.



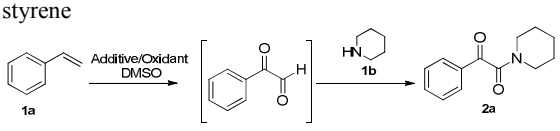
Scheme 1 One-pot synthesis of α- ketoamide from styrenes

To initiate our study, the reaction of styrene **1a** with piperidine **1b** was chosen as the model reaction in the presence of different iodine sources as additives and different oxidants. It was observed that the reaction of styrene (0.5 mmol) and piperidine (1.5 mmol) with I_2/IBX (1 mmol / 0.75 mmol) in DMSO at 70 ^oC for 6 hours afforded the desired α-ketoamide **2a** in 14% yield (Table 1, entry 1). We observed that prolonging the reaction time also did not improve the yield. However, instead of taking the reactants together, styrene and I_2/IBX were taken and heated at 70 ^oC in DMSO for 2 hours, with the subsequent addition of piperidine to the mixture and further stirring for 2.5 hours at the same temperature produced the desired product **2a** in 31% yield (entry 2).

To improve the yield of α-ketoamide further, a set of reactions were carried out (entries 3-14). First, the addition of reagent in different time interval of addition was examined. It was observed that the initial stirring of styrene with I_2/IBX at 70 ^oC in DMSO for 3.5 hours followed by drop wise addition of piperidine and further stirring for 2 hours gave 38% of **2a** (entry 3). Different temperatures were scanned to get the optimum reaction temperature. A better yield of 45% was obtained at 80 ^oC temperature (entry 4). No further increase in yield was observed at higher temperatures than 80 ^oC (entry 5). Then different peroxide based oxidants like TBHP, H_2O_2

and di *tert*-butyl peroxide (DTBP) were examined in the presence of molecular iodine and observed that only TBHP gave trace amount of product, whereas none of the other two were able to promote the reaction, resulting in no product formation even after 48 hours (entries 6-8). *N*-Iodosuccinimide (NIS) was also tried as the source of iodine with IBX and gave a moderate yield of 29% (entry 9).

Table 1 Optimization studies for one-pot synthesis of α-ketoamide from styrene



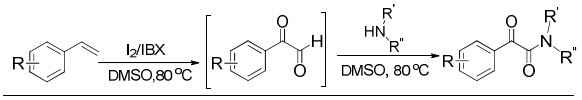
Sl. No.	Additive (mmol)	Oxidant (mmol)	Piperidine (mmol)	Temperature (°C)	Yield (%) [a]
1	I_2 (1.0)	IBX (0.75)	1.5	70	14[b]
2.	I_2 (1.0)	IBX (0.75)	1.5	70	31[c]
3.	I_2 (1.0)	IBX (0.75)	1.5	70	38
4.	I_2 (1.0)	IBX (0.75)	1.5	80	45
5.	I_2 (1.0)	IBX (0.75)	1.5	90	43
6.	I_2 (1.0)	TBHP (0.75)	1.5	80	trace[d]
7.	I_2 (1.0)	H_2O_2 (0.75)	1.5	80	n.r[d]
8.	I_2 (1.0)	DTBP (0.75)	1.5	80	n.r[d]
9.	NIS (1.0)	IBX (0.75)	1.5	80	29
10.	I_2 (1.0)	IBX (0.75)	2.0	80	54
11.	I_2 (0.75)	IBX (0.75)	2.0	80	48
12	I_2 (1.25)	IBX (0.75)	2.0	80	53
13	**I_2 (1.0)**	**IBX (1.0)**	**2.0**	**80**	**71**
14	I_2 (1.0)	IBX (1.25)	2.0	80	68
15	I_2 (1.0)	-	2.0	80	47 [e]
16	-	IBX (1.25)	2.0	80	43 [f]
17	-	-	2.0	80	n.r[g]

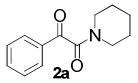
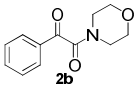
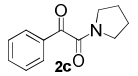
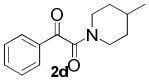
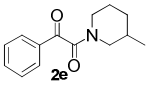
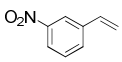
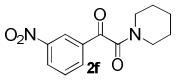
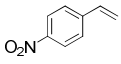
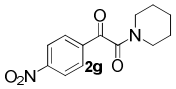
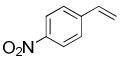
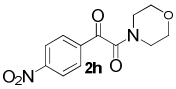
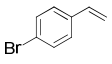
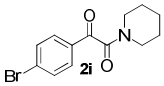
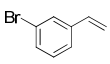
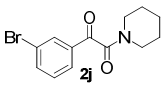
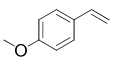
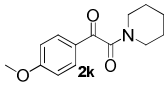
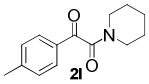
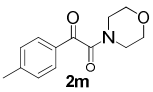
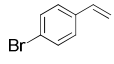
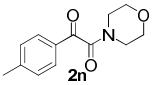
General reaction condition: **1a** (0.5 mmol), additive and oxidant were stirred in DMSO at 80 °C for 3.5 h and then **1b** was added drop wise and stirred till completion of reaction; [a]Isolated Yield; [b]Reaction condition: **1b** was added initially along with styrene; [c]Reaction condition: initially styrene, I_2/IBX mixture was stirred for 2 h and after the addition of amine reaction stirred for 2.5 h; [d]Reaction condition: reaction was run for 48 h. [e] Reaction was carried out without IBX. [f] Reaction was carried out without I_2. [g] Reaction was carried out without IBX and I_2.

Further optimization was continued with I_2/IBX, which is the optimal additive-oxidant pair for this transformation. Low solubility of IBX in solvents other than DMSO restricts its reactions in different solvents. The reaction was performed in different solvents like EtOAc, THF, MeCN and solvent mixtures like MeCN:H_2O (1:1), acetone : H_2O (86:14) and DMSO : CH_2Cl_2 (1:1) but no product was obtained in any of the solvents after continuing the reaction for 24 hours. Often to overcome the solubility barrier, different phase transfer catalysts were also used. Other solvents and *n*-Bu_4NBr is found to be one of the best suited phase transfer catalyst for IBX based reactions. Thus above mentioned solvents were tried in presence of *n*-Bu_4NBr (0.5 equiv, 0.25 mmol) and 10 equiv. of DMSO (for solvents other than DMSO: CH_2Cl_2) but none resulted in any product formation.

When the reaction was tried with one and two equiv. of piperidine in less yield or incomplete conversion of the phenylglyoxal intermediate was observed.[24] The use of 4 equiv. of piperidine was found to be the best condition for the reaction (entry 10). Subsequently, the amount of I_2 and IBX were also monitored (entries 11-14) and finally the optimal reaction condition for the reaction was turned out to be styrene (0.5 mmol) and piperidine (2 mmol) with I_2/IBX (1.0mmol/1.0mmol) at 80 °C in DMSO solvent (entry 13).

Table 2 Substrate scope of I_2/IBX promoted α-ketoamide formation



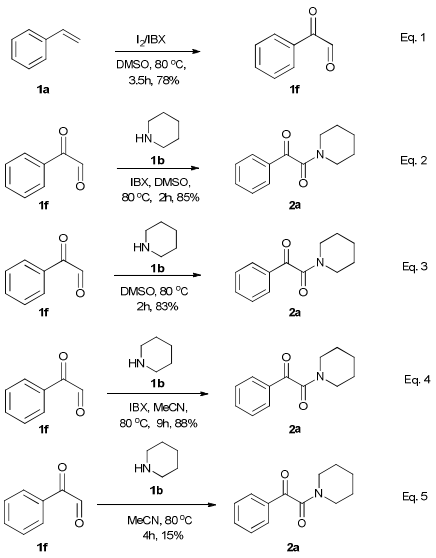
S.No.	Alkene	Product	Time (h)	Yield (%)[a]
1			7.5 (3.5+4)	71
2			6.5 (3.5+3)	67
3			8.5 (3.5+5)	62
4			9.5 (3.5+6)	70
5			11.5 (3.5+8)	62
6			16.5 (3.5+13)	56
7			12.5 (3.5+9)	58
8			13.5 (3.5+10)	52
9			11.5 (3.5+8)	59
10			10.5 (3.5+7)	52
11			11.5 (3.5+8)	67
12			6.5 (3.5+3)	62
13			7.5 (3.5+4)	64
14			8.5 (3.5+5)	58

[a] Isolated yield. General reaction condition: Alkene (0.5 mmol) with I_2/IBX (1.0 mmol/1.0 mmol) were stirred in DMSO at 80 °C for 3 h and then amine (2 mmol) was added dropwise and stirred till completion of reaction.

Following the optimal conditions, different sets of reactions were carried out to investigate the scope as well as the limitations of this methodology and the results are summarized in Table 2. Initially, different styrene derivatives were tested with piperidine under optimized condition. Styrenes with substitution at the phenyl ring

with electron withdrawing as well as electron donating groups such as methyl, methoxy, bromo, and nitro groups were examined and corresponding products were obtained with 56-67% yield (entries 6-14). In addition, several amines were also tried taking styrene as the terminal alkene. Piperidine, pyrrolidine and morpholine as the source of amines gave corresponding products in moderate to good yields (entries 1-3). However, aliphatic primary amine such as *N*-butyl amine, aromatic primary amine such as aniline and aromatic secondary amines like *N,N*-diphenylamine and *N*-methyl aniline were unable to produce the desired products even keeping them for more than 48 hours under optimized reaction conditions. From the above mentioned experimental results it can be concluded that this method is only applicable with aliphatic secondary amines as supported by the Stark enamine reaction which goes *via* iminium ion intermediate.[25, 26] On the other hand, non-reactivity of the aromatic secondary amines may be attributed to its decreased nucleophilicity.

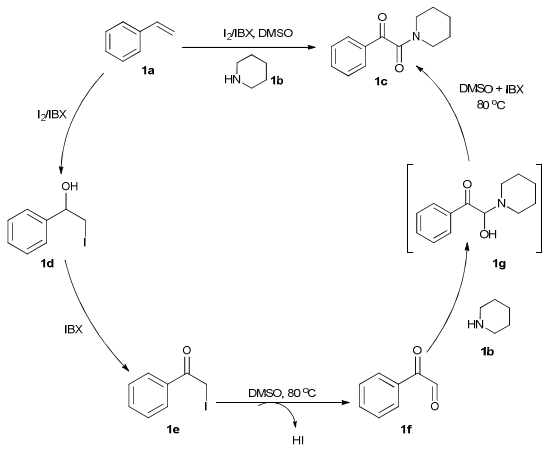
To gain insight into the reaction mechanism, control experiments were performed (Scheme 3). When the styrene was treated with optimized amount of I_2 and IBX at 80 ^oC temperature in DMSO without the addition of amine, it gave phenylglyoxal *via* the intermediates halohydrin and phenacyl iodide which were isolated and characterised (Eq. 1). This is also supported by previous reports.[27]



Scheme 3 Control experiments

When phenylglyoxal was separately treated with the optimized equivalence of piperidine, the reaction was completed within 2 hours in presence of IBX in DMSO at 80 ^oC (Eq. 2). To emphasize our hypothesis about the role of IBX in the oxidative amidation step, the same reaction was repeated in absence of IBX. Surprisingly, the reaction took place and 83% of the product **2a** formed (Eq. 3). This result suggests that DMSO acts as a promoter in the amide C-N bond formation, which is matching with literature reports.[28] But, this observation does not completely disprove the possibility of IBX acting as an oxidant in C-N bond formation. The reaction was repeated in polar aprotic solvent acetonitrile in presence of IBX and standing on our expectation, reaction completed within 9 hours (Eq. 4). Whereas, in only acetonitrile even after 72 h the conversion was very less (Eq. 5). It suggests that IBX also promotes the reaction, may be by oxidizing the intermediate hemiaminal formed.

On the basis of the control experiments and previous reports, a plausible mechanism is proposed in Scheme 4. In presence of I_2/IBX, which generates IOH *in situ*,[29] the styrene forms the halohydrin **1d** which in turn is oxidized to phenacyl iodide **1e** followed by DMSO mediated oxidation to form phenylglyoxal **1f**. It is important to mentioned that we have isolated both **1d** and **1e** during the course of the reaction. This makes DMSO an integral part of the reaction. Finally, the phenylglyoxal couples with the amine, promoted by DMSO and IBX may be by oxidizing the iminium ion and hemiaminal intermediates respectively, which might exist in equilibrium, to form the desired α-ketoamides.[30]



Scheme 4 Plausible reaction mechanism

Conclusions

In conclusion, we have developed a metal free one-pot strategy for the synthesis of α-ketoamides from readily available terminal alkenes (styrenes). The uniqueness of the method can be attributed to the use of strenes, for the synthesis of biologically and functionally important α-ketoamides. Use of amines and cost effective oxidizing agent IBX under one-pot reaction condition avoiding possibility of metal related contamination makes is suitable for synthesis related to pharmaceuticals.

Typical Experimental procedure

General Considerations

All reactions were carried out in reaction tubes under aerobic atmosphere unless otherwise mentioned. All the solvents were purchased from commercial sources and used without further purification. Wherever necessary, the solvents were dried by standard literature procedures. Reactions were monitored by thin-layer chromatography (TLC) using Merck silica gel 60 F_{254} precoated plates (0.25 mm) and analyzed by UV fluorescence quenching using appropriate mixture of ethyl acetate and hexanes as eluting solvent mixture. Silica gel (particle size 100-200 mesh) purchased from SRL India was used for column chromatography using hexanes and ethyl acetate mixture as eluent. All the chemicals used are purchased from commercially available sources and used without further purification unless otherwise mentioned. IBX was prepared using literature procedure.[31] Reactions were carried out in temperature controlled IKA magnetic stirrers. ^1H and ^{13}C NMR

spectra were recorded on a Bruker 400 or 500 MHz instrument. ^{1}H NMR spectra were reported relative to Me_4Si (δ 0.0 ppm) or residual $CHCl_3$ (δ 7.26 ppm). ^{13}C NMR were reported relative to $CDCl_3$ (δ 77.16 ppm). FTIR spectra were recorded on a Nicolet 6700 spectrometer and were reported in frequency of absorption (cm^{-1}). High resolution mass spectra (HRMS) were recorded on Q-Tof Micro mass spectrometer.

Typical experimental procedure for α-ketoamides from styrenes

In a clean reaction tube, I_2 (254 mg, 1.0 mmol) and IBX (280 mg, 1.0 mmol) was taken and dissolved in 2.5 mL of DMSO by stirring for 5 min at rt followed by addition of styrene (**1a**, 0.05 mL, 0.5 mmol). The mixture was transferred to a 80 ^{o}C oil bath and stirred for 3.5 hours. Piperidine (**1b**, 0.2 mL, 2.0 mmol) was added to the stirring solution slowly and stirred till the reaction was complete. Completion of reaction was monitored using TLC by checking the complete disappearance of the intermediate phenylglyoxal (**1f**). The reaction was then extracted with ethyl acetate for few times and the combined organic layer was washed with saturated sodium thiosulphate and saturated sodium bicarbonate solutions. It was then dried over anhydrous sodium sulphate, filtered and concentrated under reduced pressure. The crude product was purified using column chromatography (silicagel, petroleum ether:ethyl acetate=85:15) to give the desired tertiary α-ketoamide (**2a**). The data for α-ketoamides **2a-2e**[32], **2f-2i**,[33] **2j**[34], **2k-2m**[35], **2n**[33] and **1e**[36] are already reported in literature.

Acknowlegment

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Notes and references

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Electronic Supplementary Information (ESI) available: R_f values, IR, NMR and MS data for all the products and copy of ^{1}H and ^{13}C spectra for all the compounds are included in the ESI. See. DOI: 10.1039/c000000x/data.

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