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Metal-free I_2-Catalyzed Difunctionalization of terminal Alkenes: A Convenient Approach to α-Ketoamides

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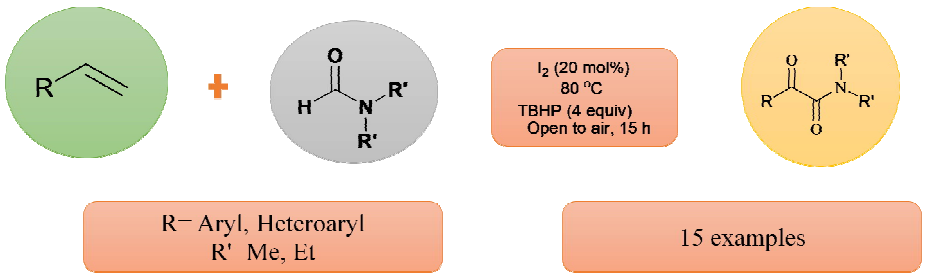
ABSTRACT

A novel and efficient one-pot operation for the synthesis of α-Ketoamides has been reported via difunctionalization of terminal alkenes using I_2 as a mild catalyst in open atmospheric condition. The metal-free approach utilizing TBHP as an oxidant makes our protocol economically and environmentally benign.

graphical Abstract



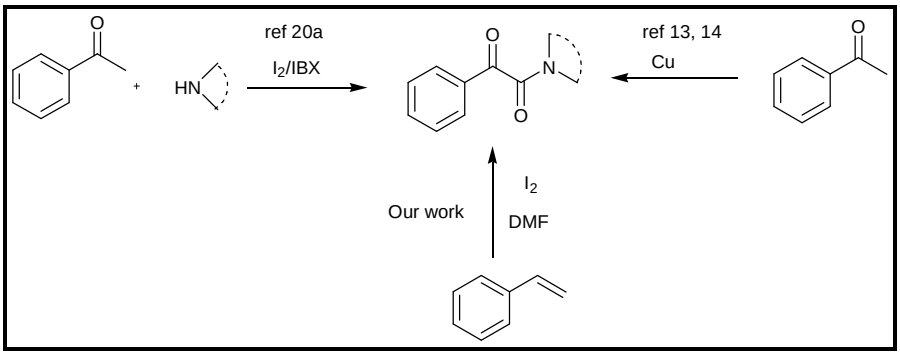
Keywords: α-Ketoamides, Alkenes, I_2 catalysis, Radicals, Aerobic oxidation

INTRODUCTION

As pervasive structural moieties in a widespread number of pharmaceuticals compounds, α-Ketoamides posses a promising role in drugs and natural products. In addition, it also acts as anticancer agents, HIV inhibitors, FIV protease inhibitors and histone deacetylase inhibitors [**1-6**]. The moiety of α-Ketoamides also attributes to the activities of transition state inhibitory immunosuppressive drugs like tacrolimus and sirolimus [**7, 8**]. Although it has a wide and efficient role in biological activities it is also an important intermediate in organic synthesis and functional group transformation [**9, 10**]. Hitherto, several synthetic strategies have been developed considering the importance of α-Ketoamides scaffolds. Among them, the most common and widely used method includes amidation of α-Ketoacids and α-Keto acyl halides

[**11**]. Metal catalyzed methodologies have overcome the drawbacks of these traditional methods. Among which Palladium-catalyzed double carbonylation of aryl halides [**12**], copper-catalyzed oxidative synthesis of α-Ketoamides from ketones [**13, 14**], and dehydrogenative coupling of amine and α-carbonyl aldehyde *etc*., [**15**] have inspired many chemists for the synthesis of tertiary α-Ketoamides (Scheme 1). Although efficient in many aspects, these expensive transition metals being hazardous, toxic in nature and sensitive to moisture and air increases the demand for metal-free methodologies.

According to recent literature, aryl methyl ketone, terminal alkynes and oxoaldehyde [**16b**] have proved to be a common efficient substrate for metal-free approach to α-Ketoamides [**16-19**]. Alkenes have been used extensively as a substrate for organic synthesis due to it's readily availability and versatility. Recently, Sekar *et. al*. have discovered I_2/IBX promoted synthesis of α-Ketoamides from alkenes [**20a**]. However, the lower solubility of IBX and its shock sensitivity limits the availability of this methodology. Deshidi *et al*., have synthesized α-Ketoamides using DMSO and equivalent amount of I_2 [**20b**]. Guo and co-workers have also developed I_2-promoted aerobic oxidative coupling of acetophenones with amines to give α-Ketoamides [**21**]. In spite of being metal-free and appealing approach, a need for a catalytic platform still creates an opportunity to develop a novel, simple and highly efficient synthetic route for one-pot synthesis of α-Ketoamides.



Scheme 1. Synthesis of α-Ketoamides

Radical chemistry has received a lot of attention in organic synthesis due to its mild, efficient and environmentally benign nature. [**22, 23**] Inspired by the upcoming work of the radical initiated synthesis and our continuous effort on the difunctionalization of alkenes [**24**], lead us to propose an efficient, simple and mild pathway for the synthesis of α-Ketoamides utilizing easily available alkenes and dimethylformamide as a source of amine radical. It's a new method of C-N bond formation via decarbonylation [**23**].

MATERIALS AND METHODS

^{1}H NMR spectra were recorded on a Bruker Avance II (400 MHz) FT spectrometer in $CDCl_3$ using TMS as internal reference. ^{13}C NMR spectra were recorded on the same instrument at 100 MHz in $CDCl_3$ and TMS was used as internal reference. All coupling constant (*J*) are reported in Hertz (Hz). Mass (EI) spectra were recorded on JEOL D-300 mass spectrometer. Melting points were determined by open glass capillary method and are uncorrected. All chemicals used were reagent grade and were used as received without further purification. All reactions were performed using oven-dried glassware. Organic solutions were concentrated using a Buchi rotary evaporator. Column chromatography was carried out over silica gel (Merck 100–200 mesh) and TLC was performed using silica gel GF254 (Merck) plates.

General Procedure for the synthesis of α-Ketoamides 3: A mixture of aryl terminal alkene **1** (1 mmol), I_2 (20 mol%) and TBHP (4 mmol) in dialkylformamide (3 mL) was stirred at 80°C temperature for 15 h under atmospheric air in a round bottom flask. After completion of the reaction as monitored by TLC, water (5 mL) was added and the mixture was extracted with ethyl acetate (3 X 5 mL). The combined organic phases were dried over anhyd. sodium sulphate, filtered and concentrated under reduced pressure. The residue obtained was purified by column chromatography using a gradient mixture of *n*-hexane/ethyl acetate as eluent to obtain an analytically pure sample of α-Ketoamides **3** (Table 2, entries 3a-o) in 76-89% yields.

Characterization Data of Representative Compounds

***N, N*-dimethyl-2-oxo-2-phenylacetamide (Table 2, entry 3b):** (Colourless liquid) IR (KBr): 1680, 1644. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 7.95-7.98 (m, 2H), 7.61-7.66 (m, 1H), 7.51-7.53 (m, 2H), 3.15 (s, 3H), 3.00 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 191.9, 167.0, 134.8, 133.0, 129.5, 128.9, 36.9, 33.9. EIMS (m/z): 177 (M^+). Anal.calcd for $C_{10}H_{11}NO_2$: C, 67.78; H, 6.26; N, 7.90. Found, C, 67.89; H, 6.32; N, 7.85.

2-(4-fluorophenyl)-*N, N*-dimethyl-2-oxoacetamide (Table 2, entry 3e): (Colourless liquid) IR (KBr): 1679, 1645. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 8.00-8.05 (m, 2H), 7.13-7.20 (m, 2H), 3.13 (s, 3H), 3.00 (s, 3H) ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 189.9, 168.0, 166.8, 165.5, 132.3, 129.5, 116.3, 116.3, 29.9, 33.9. EIMS (m/z): 195 (M^+). Anal.calcd for $C_{10}H_{10}FNO_2$: C, 61.53; H, 5.16; N, 7.18 Found, C, 61.40; H, 4.98; N, 7.07.

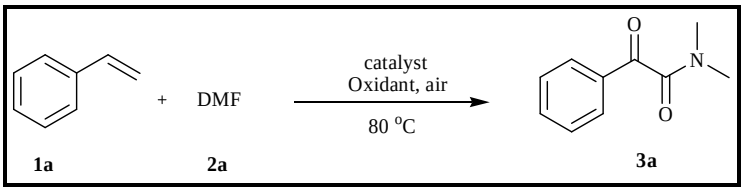
2-(furan-2-yl)-*N, N*-dimethyl-2-oxoacetamide (Table 2, entry 3k): (Colourless liquid) IR (KBr): 1694, 1650. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 7.69 (s, 1H), 7.40 (s, 1H), 6.64 (s, 1H), 3.12 (s, 3H), 3.00 (s, 3H) ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 178.6, 165.3, 150.3, 148.8, 122.5, 112.9, 37.1, 34.4. EIMS (m/z): 168 (M^+). Anal.calcd for $C_8H_9NO_3$: C, 57.48; H, 5.43; N, 8.38; Found, C, 57.69; H, 5.55; N, 8.46.

***N, N*-diethyl-2-(4-nitrophenyl)-2-oxoacetamide (Table 2 entry 3o):** (Colourless liquid) IR (KBr): 1690, 1643. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 8.37 (d, J = 7.2Hz 2H), 8.12 (d, J = 7.2Hz, 2H), 3.60 (q, J = 7.2Hz, 2H), 3.30 (q, J =7.2Hz, 2H), 1.28 (t, J = 7.2Hz, 3H), 1.21 (t, J = 7.2Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ =189.0, 165.5, 149.9, 137.8, 130.6, 124.0, 42.2, 39.4, 14.4, 12.7. EIMS (m/z): 250 (M^+). Anal.calcd for $C_{12}H_{14}N_2O_4$: C, 57.59; H, 5.64; N, 11.19. Found, C, 57.64; H, 5.34; N, 10.98.

RESULTS AND DISCUSSION

Initially, we envisaged the synthesis of α-Ketoamides via I_2 catalyzed difunctionalization of alkenes with DMF in the air atmosphere. We proceeded with a model reaction of styrene **1a** (1 mmol) and iodine (20 mol%) in DMF **2a** (3 mL) using TBHP (4 mmol) as an oxidant at 80°C. To our delight, 88% of **3a** was obtained. With this excellent yield in our hand, we further proceeded to optimize our reaction condition by carrying a series of control experiments. In the absence of either catalyst or oxidant no product formation was observed (Table 1 entries 7, 8). Among various catalyzing reagent used like I_2, $PhI(OAc)_2$, nBu$_4$NI, and nBu$_4$NBr, I_2 proved to be the best (Table 1, entries 1,10-12). Next, we observed that on decreasing 20 mol% of I_2 to 10 mol% the product yield also decreased to 70% (Table 1, entry 2). Further, when it was increased from 20 mol% to 30 mol% there was no change observed in yield (Table 1, entry 3). No product was observed when the reaction was carried out under the inert N_2 atmosphere (Table 1, entry 9), this revealed the necessity of O_2 for the formation of α-Ketoamides. Various oxidants were also examined such as DTBP, H_2O_2, and $K_2S_2O_8$ but none of them were suitable for our standard reaction condition (Table 1, entries 4-6). The yield was reduced to 55% on decreasing TBHP to 2 equiv. (Table 1, entry 13).

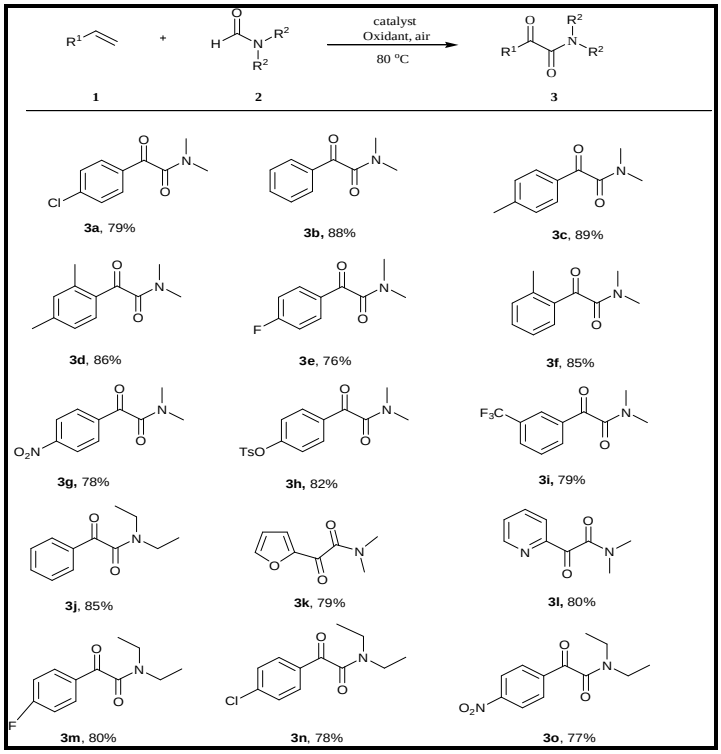
Table 1. Optimization of reaction conditions[a]



Entry	Catalyst (mol%)	Oxidant (mmol)	Time (h)	Yield (%)[c]
1	I_2 (20)	TBHP (4)	15	88
2	I_2 (10)	TBHP (4)	15	70
3	I_2 (30)	TBHP (4)	15	88
4	I_2 (20)	DTBP (4)	15	5
5	I_2 (20)	H_2O_2 (4)	15	1
6	I_2 (20)	$K_2S_2O_8$ (4)	15	-
7	I_2 (20)	-	15	n.r.
8	-	TBHP (4)	15	n.r.
9[b]	I_2 (20)	TBHP (4)	15	-
10	$PhI(OAc)_2$ (20)	TBHP (4)	15	20
11	nBu_4NI (20)	TBHP (4)	15	10
12	nBu_4NBr (20)	TBHP (4)	15	Traces
13	I_2 (20)	TBHP (2)	15	55

[a]Reaction conditions: Styrene (1 mmol), catalyst (mol%), DMF(3 mL)Oxidant (4 mmol) under an air atmosphere at 80°C
[b] Reaction carried under inert N_2 atmosphere
[c] Isolated yield of **3a** after flash chromatography

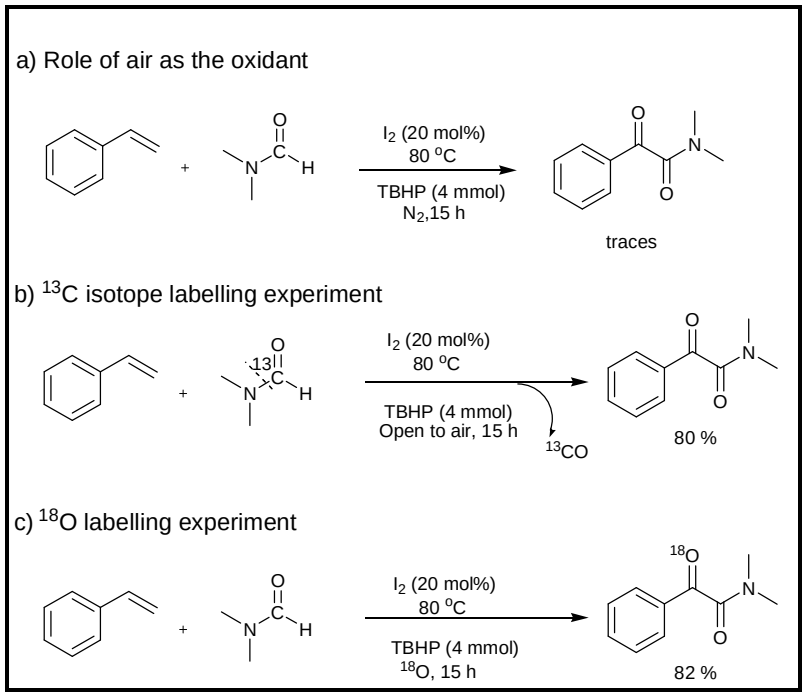
Table 2. Difunctionalization of terminal alkenes with dialkylformamides to yield α-Ketoamides[a]



[a] Reaction conditions: aryl terminal alkene (1 mmol), dialkylformamide (3 ml), I_2 (20 mol%) TBHP (4 mmol), 80°C, open-air condition, 15 h
[b]All compounds are known and gave C, H and N analyses within ±0.37% and satisfactory spectral (IR, ^{1}H NMR, ^{13}C NMR and EIMS) data with those reported in the literature [**16, 20, 21, 24d, 27**]

Whereas, 4-fluro-phenyl styrene **1e** treated with DMF **2a**, the yield of α-Ketoamide **3e** slightly decreased to 76%. Even heteroaryl terminal alkene (**1k, 1l**) also produced 79-80% of α-ketomide in the present reaction condition (Table 2 **3k**, **3l**). The scope of the reaction was also observed with *N*, *N*-diethylformamide **2b** and could be easily transformed into our desired product in average to good yield (**3j**, **3m-3o**).

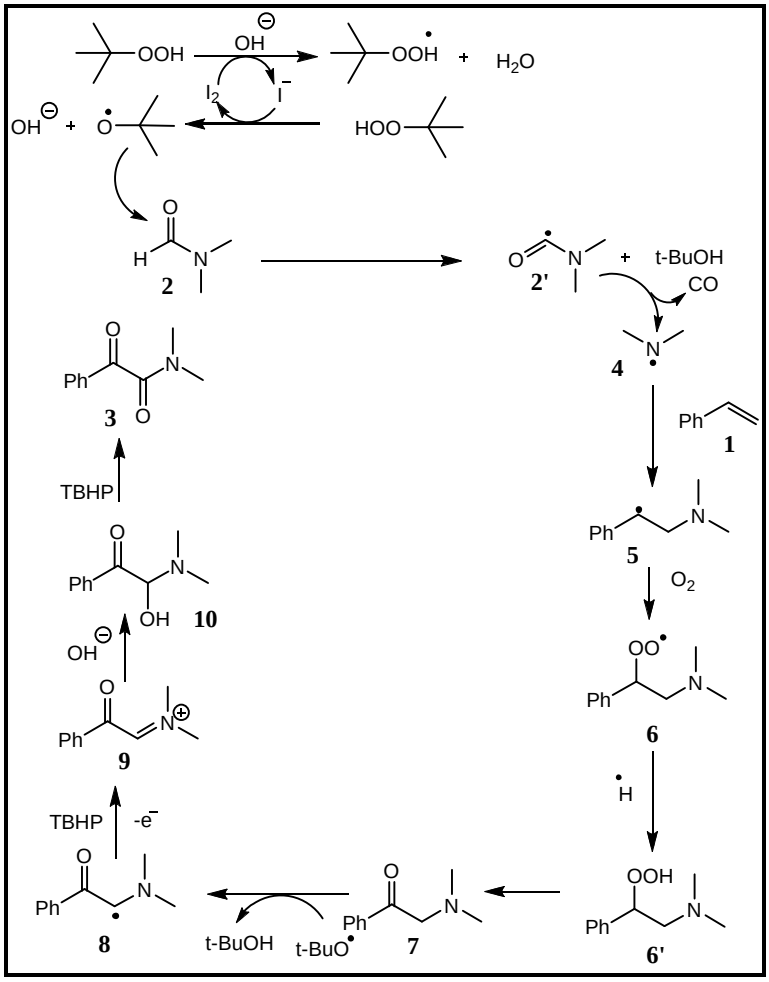
A number of experiments were performed to investigate a plausible reaction pathway as shown in Scheme 2.



Scheme 2. Mechanistic investigation.

The role of O_2 was studied by performing the reaction under N_2 condition. The reaction was inhibited in the given condition (Scheme 2a). Next, on further carrying out ^{13}C-isotope labelling experiment proves that the acyl group didn't come from the DMF (Scheme 2b). ^{18}O-isotope containing α-Ketoamides was obtained in 82 % yield (Scheme 2c) confirming the attack of dioxygen [**24c**]. It is the first report of difunctionalization of alkene via decarbonylation of DMF in air atmosphere under metal-free condition [**25**].

On the basis of the above results and literature precedents [**16, 24d, 26-27**] a plausible reaction mechanism for the formation of α-Ketoamides **3** has been shown in Scheme 3. Firstly I_2 catalyzes the formation of tert- butyl peroxyl and tert-butoxyl radicals. This tert-butoxyl radical abstracts hydrogen from **2** to form acyl radical **2'** which further forms aminyl radical **4** by decarbonylation. Next, a carbon-centered radical **5** is formed by the attack of aminyl radical on **1**. The addition of dioxygen on **5** produces **7** which on oxidation with TBHP yield **10** which further oxidized to give the desired product **3**.



Scheme 3. Plausible reaction pathway for the formation of α-Ketoamides

APPLICATION

The synthesis of α-Ketoamides using terminal alkene with DMF is very facile and eco-friendly method and is present in many bio-active molecules. The use of iodine as a catalyst is easily available and non toxic in nature. This method develops C-N bond formation in terminal alkene utilizing DMF both as a solvent and reactant. It has a great application in medical and pharmaceuticals field. This novel methodology also plays an important role in drugs synthesis.

CONCLUSION

α-Ketoamides has been synthesized via a novel approach of difunctionalization of terminal alkenes in a metal-free condition in the air atmosphere utilizing TBHP as an oxidant. This protocol is thus environmentally friendly and a new method to synthesis of α-Ketoamides.

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