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Metal-Free Tandem Oxidative Aryl Migration and C−C Bond Cleavage: Synthesis of α-Ketoamides and Esters from Acrylic Derivatives

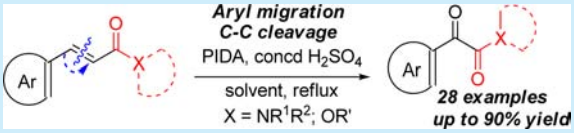
Le Liu,[†] Liang Du,[†] Daisy Zhang-Negrerie,[†] Yunfei Du,*[,†,‡] and Kang Zhao*[,†]

[†]School of Pharmaceutical Science and Technology, Tianjin University, Tianjin 300072, China

[‡]Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300072, China

Supporting Information

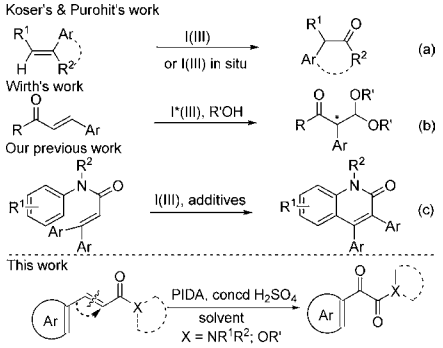
ABSTRACT: A novel tandem metal-free oxidative aryl migration/C−C bond-cleavage reaction, mediated by hypervalent iodine reagent, has been discovered. The presented transformation provided straightforward access to important α-ketoamide and α-ketoester derivatives from readily available acrylic derivatives via a concerted process of 1,2-aryl shift concomitant with C−C bond cleavage.



Functionalization of alkenes represents one of the most challenging processes and remains a central topic in organic chemistry.[1] Oxidative rearrangement, as one of the most impressive branches of these transformations, permits rapid and efficient constructions of complex molecules from simple building blocks.[2] Consequently, considerable efforts have been devoted to the area of oxidative rearrangement.[3] Most of the existing methods are attractive in their effectiveness and efficiency but are unfortunately associated with the limitation of the involvement of transition metals such as Cr,[3a] Pt,[3b] Rh,[3c−f] Cu,[3g−i] and Pd.[3j−l] Despite the progress in developing mild and metal-free procedures[4] in recent decades, examples of environmentally green methods are still limited in number.

Hypervalent iodine reagents,[5] readily available, nontoxic, and environmental benign, have been reported to act as electrophiles to activate the double bonds in alkenes,[6] which initiate oxidative rearrangement through ring expansion,[7] ring contraction,[8] or aryl migration.[6b−d,m] Koser's group[6f] reported the first hydroxytosyloxy iodobenzene (HTIB)-mediated oxidative rearrangement of 1,1-diphenylethylene, which later expanded to a versatile type of arylalkenes and cyclic arylalkenes.[6g] Purohit and co-workers[6h] demonstrated an efficient catalytic use of iodine compounds which generated I(III) in situ to furnish the oxidative 1,2-aryl shift of 1,1-disubstituted olefins (Scheme 1, a). Wirth and co-workers reported the first stereoselective rearrangements of alkenes with high enantioselectivities by chiral hypervalent iodine reagents (Scheme 1, b).[6c] A short while ago, we also disclosed a novel access to 3-arylquinolinones from *N*-phenylcinnamamide via oxidative aryl migration and cyclization (Scheme 1, c).[6m] Hypervalent iodine reagents are also known to be used as potent oxidants to realize the cleavage of alkene C═C to form carbonyl compounds.[9] Nevertheless, a carful survey of the literature shows no report on oxidative rearrangement involving C−C double-bond cleavage under metal-free conditions. We herein report, as a continuous part of our work on hypervalent iodine chemistry,[10] the discovery of a novel I(III)-mediated tandem oxidative rearrangement and C−C bond cleavage reaction of acrylic derivatives. To our knowledge, this is an unprecedented metal-free protocol for the synthesis of α-ketoamide and esters from acrylic derivatives featuring a cascade oxidative rearrangement and C−C bond-cleavage process.

Scheme 1. Hypervalent Iodine Reagent Mediated Oxidative Rearrangement of Alkenes



In an effort to systematically investigate and gain insight of the transformations for the synthesis of 3-arylquinolinones,[6m] we designed and synthesized *N*,*N*-diethylcinnamamide (**1a**), which replaced the aniline moiety on the substrate (*N*-methyl-*N*-phenylcinnamamide) with an alkylamine. However, much to our delight, we found that when **1a** was subjected to the conditions we developed for the synthesis of 3-arylquinolinones, an unexpected *N*,*N*-diethyl-2-oxo-2-phenylacetamide was obtained in 25% yield (Table 1, entry 1). We were then sidetracked to explore this novel transformation, a worthwhile pursuit in our opinion, as not only was the product generated a useful skeleton in many natural products, pharmaceuticals, and intermediates in organic synthesis[11] but also the concerted nature of the process

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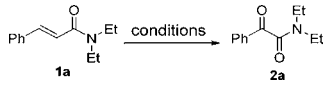
Table 1. Optimization of the Reaction Conditions[a]



entry	solvent	oxidant (equiv)	additive (equiv)	time (h)	yield[b] (%)
1	DCE	PIFA (2.0)	$BF_3{\cdot}Et_2O$/TFA	24	25
2	DCE	PIFA (3.0)	$BF_3{\cdot}Et_2O$/TFA	20	43
3	DCE	PIFA (3.0)		24	NR
4	DCE	PIFA (3.0)	$NaHSO_4$ (1.0)	15	49
5	DCE	PIFA (3.0)	NH_4HSO_4 (1.0)	12	64
6	DCE	PIFA (3.0)	H_2SO_4 (1.0)	1	73
7	EA	PIFA (3.0)	H_2SO_4 (1.0)	5	82
8	MeOH	PIFA (3.0)	H_2SO_4 (1.0)	10	NR
9	CH_3CN	PIFA (3.0)	H_2SO_4 (1.0)	24	55
10	DMF	PIFA (3.0)	H_2SO_4 (1.0)	24	NR
11	TFE	PIFA (3.0)	H_2SO_4 (1.0)	10	70
12	EA	PhIO (3.0)	H_2SO_4 (1.0)	24	20
13	EA	PIDA (3.0)	H_2SO_4 (1.0)	10	88
14[c]	DCM	PIDA (3.0)	H_2SO_4 (1.0)	7	90

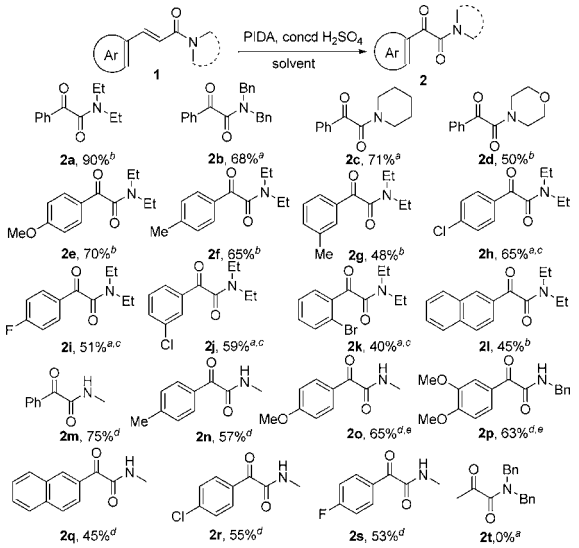
[a]All reactions were carried out with **1a** (0.4 mmol) and oxidant in solvent (c = 0.05 M) under air, and the H_2SO_4 used is 98% (m/m). [b]Isolated yields. [c]$BF_3{\cdot}Et_2O$ (1.0 equiv) was added. NR = no reaction occurred.

involving an oxidative rearrangement and C−C bond cleavage appeared fascinating to us.

We began by optimizing the reaction conditions, the results of which are shown in Table 1. Increasing the loading of PIFA to 3.0 equiv led to a complete consumption of the starting material and an overall yield of 43% (Table 1, entry 2). Further screening indicated that acidic additive was essential to this reaction since the use of H_2SO_4 as an additive had dramatically facilitated the transformation leading to a significantly improved yield of 73% (Table 1, entries 1−6). Subsequently, the effect of solvent on the reaction was evaluated. Among the solvents tested, ethyl acetate was found to be superior to all the other solvents such as DCE, MeOH, CH_3CN, DMF, and TFE, resulting in an 82% yield of the desired product (Table 1, entries 7−11). Among alternative hypervalent iodine reagents investigated, iodosobenzene (PhIO) was less effective with only 20% of the product isolated, while PIDA provided a slightly higher yield of 88% (Table 1, entries 12 and 13). In addition, a similar high yield was obtained when PIDA was used as the oxidant in the presence of H_2SO_4 and $BF_3{\cdot}Et_2O$ in DCM at room temperature (Table 1, entry 14).

With the optimized conditions in hand, a series of acrylic amides were synthesized to investigate the scope and generality of the method. The established parameters of reaction conditions were proven to be generally effective for a wide range of substrates. A variety of amines, specifically those with the diethylamine replaced by dibenzylamine, piperidine, or morpholine, all reacted under the optimal reaction conditions (Scheme 2). The corresponding 2-oxo-2-phenylacetamides were afforded in satisfactory yields (**2a**−**d**). Moreover, the method was to extend to phenyl groups bearing both electron-donating (methyl and methoxyl) and -withdrawing (halogens) substituents, and the resulting products were obtained in 40−70% yields (**2e**−**g**, **i**−**l**). It should be mentioned that the *para*-substituted substrates, with either an electron-donating or -withdrawing group, underwent the oxidative migration/C−C double-bond cleavage process more smoothly and efficiently than the *meta*-substituted substrates and much more so than the *ortho*-substituted

Scheme 2. PIDA-Mediated Oxidative Rearrangement and C−C Bond Cleavage of Acrylic Amides[a]



[a]Conditions A: **1** (0.4 mmol), PIDA (1.2 mmol), concd H_2SO_4 (0.4 mmol) refluxing in ethyl acetate under air; isolated yields are given. [b]Conditions B: **1** (0.4 mmol), PIDA (1.2 mmol), concd H_2SO_4 (0.4 mmol), $BF_3{\cdot}Et_2O$ (0.4 mmol) in DCM at rt under air; isolated yields are given. [c]$BF_3{\cdot}Et_2O$ (0.4 mmol) was added to the reaction. [d]TFE was used as the solvent under reflux. [e]Reaction temperature was between −20 °C and rt.

substrates, which not only required longer reaction time but suffered decreased yield (**2f**−**k**). These observations indicate that steric hindrance probably plays a role in the transformation process. The reactivity of 3-(naphthalen-2-yl)acrylic amide was also demonstrated, and the corresponding product was obtained in 45% yield (**2l**). Moreover, the monosubstituted NH free cinnamamides were also shown to be tolerable under the optimal conditions, and the corresponding NH free α-ketoamides were delivered in fair to good yields (**2m**−**s**). We also attempted to extend this protocol to alkyl-substituted acrylic amide. Disappointingly, compound **1t** was proven to be inert to the standard conditions, yielding no desired product **2t**.

Then, the reactivity of a variety of substituted acrylates was tested for the protocol. To our delight, when the readily available methyl cinnamate **3a** was subjected to slightly modified reaction conditions employing TFE as the solvent, the reaction proceeded smoothly and produced the corresponding ester in 75% yield (Scheme 3, **4a**). Moreover, both benzyl and isopropyl cinnamates were tolerated and the desired α-ketoesters were isolated in 52% and 65% yields, respectively (Scheme 3, **4b** and **4c**). Methyl cinnamates bearing both electron-donating and -withdrawing groups, even 3-(naphthalen-2-yl)acrylate, were all tolerated, affording the corresponding aryl migrated and C−C double bond cleaved products in acceptable yields (Scheme 3, **4d**−**g**). On the other hand, the low yield of the products could be attributed to the transeterification reactions between the desired product and the solvent. The corresponding 2,2,2-trifluoroethyl-α-ketoesters were detected by crude ^{19}F NMR, and the transesterificated product derived from **4f** and TFE was isolated in 15% yield.

On the basis of the experimental results and literature overview, a plausible mechanism was proposed (Scheme 4). It is well-known that hypervalent iodine reagent could be activated by Lewis acid or Bronsted acid.[6e,12] Thus, we assumed that PIDA was first activated by protonation with H_2SO_4, which increased

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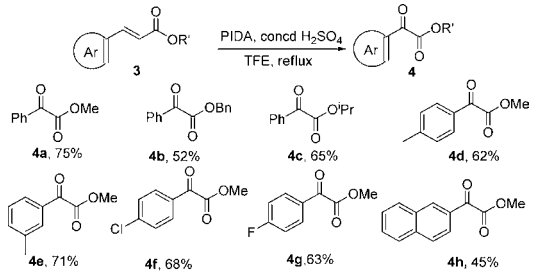
Scheme 3. PIDA-Mediated Aryl Migration and C−C Bond Cleavage of Acrylates[a]

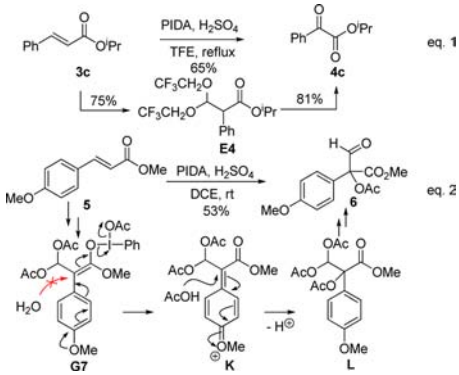


[a]All reactions were carried out with **3** (0.4 mmol), PIDA (1.2 mmol), concd H_2SO_4 (0.4 mmol) with refluxing in TFE under air; isolated yields are given.

the electrophilicity of the iodine center. Then the nucleophilic attack on the iodine center by the carbonyl oxygen of the amide moiety in **1a** afforded iminium salt **A**, the resonance structure of which, namely, the benzyl cation **B**, was subsequently trapped by acetate acid to give intermediate **C**. Assisted by the oxygen lone pair conjugation, the phenyl group migrated with the release of phenyl iodide to generate oxonium **D**, which was attacked by another acetate to give intermediate **E**. Oxidation of **E** by activated PIDA in a similar fashion generated iminium salt **F** which lost one proton to afford **G**. Nucleophilic attack of the alkene by water, along with the elimination of iodobenzene and acetic acid, gave the oxidized alcohol **H**, which was further oxidized by a third equivalent of PIDA to furnish intermediate **I**. Acetic acid attacked the electrophilic carbonyl carbon in the ester part of **I** afforded hemiketal **J**. Finally, fragmentation of **J** led to the cleavage of C−C bond and C−I bond, resulting in the formation of **2a** and acetic formic anhydride.[13]

In allusion to the proposed mechanism, additional experiments were conducted, the results of which were all supportive of the mechanism, even though some of them yielded unexpected products at first sight. When isopropyl cinnamate **3c** was treated with PIDA in the presence of H_2SO_4 under refluxing in TFE for 24 h, the reaction proceeded smoothly and gave the expected α-ketoester **4c** in moderate 65% yield. However, 7 h after the reaction was set, an intermediate product, isopropyl 2-phenyl-3,3-bis(2,2,2-trifluoroethoxy)propanoate **E4** was successfully isolated in 75% yield. Taking pure **E4** as the starting material and subjecting it to the standard conditions, **4c** was obtained in an expected yield of 81% (65%/75% is roughly 87%) (Scheme 5, eq 1). This observation of **E4** gives unambiguous evidence of the existence of **E** as suggested by the mechanism. The subtly structural difference between **E4** and **E** can be attributed to competition for trapping the generated cation intermediate **D**

Scheme 5. Some Experimental Evidence of the Mechanism



between the nucleophilic solvent TFE and the released acetic acid. Such competition is absent in cases where ethyl acetate or DCE was employed as the solvent. More evidence came from fact that when *p*-OMe cinnamate **7** was treated with PIDA in the presence of H_2SO_4 in DCE an unexpected product, aldehyde **6**, was isolated in moderate 53% yield (Scheme 5, eq 2). We reasoned that cinnamate **5** underwent the same mechanistic pathway and formed a **G**-like intermediate **G7**. At this point, instead of being nucleophilically attacked by a water molecule, it was attacked by acetic acid, a normally weaker nucleophile but facilitated in this case by the intermediate oxonium **K** generated due to the electron-donating methoxy group, in exchange for a stronger C−O bond and therefore thermodynamically more stable molecule. Hydrolysis of the diacetate **L** led to the formation of the isolated aldehyde **6**.

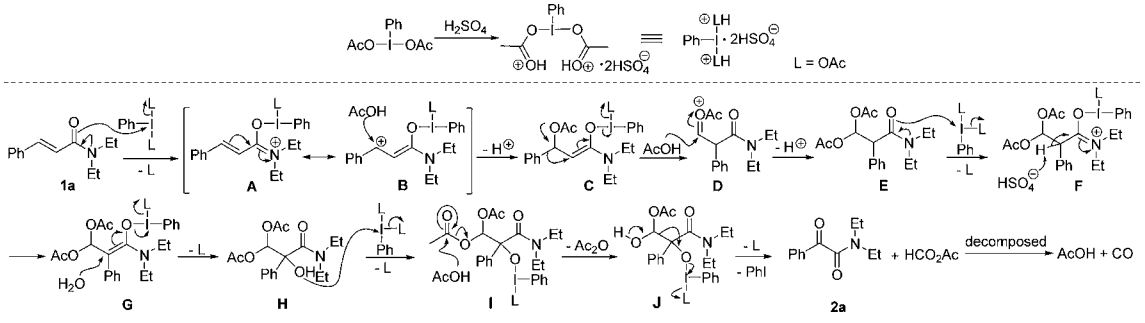
In conclusion, we have developed a novel metal-free oxidative protocol for the synthesis of α-ketoamides and esters from readily available acrylic derivatives. The procedure, mediated by the mild hypervalent iodine reagent, features a tandem oxidative aryl migration and C−C double bond cleavage process. To our knowledge, this is the first example of a concerted process involving both oxidative aryl migration and C−C bond cleavage. The detailed mechanistic insight for the transformation is under investigation in our research group.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedure, new compound characterization data, and NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

Scheme 4. Proposed Mechanism



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AUTHOR INFORMATION

Corresponding Authors

*E-mail: duyunfeier@tju.edu.cn.
*E-mail: kangzhao@tju.edu.cn.

Notes

The authors declare no competing financial interest.

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