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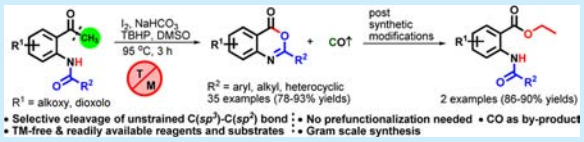
Selective Oxidative Decarbonylative Cleavage of Unstrained C(sp^3)–C(sp^2) Bond: Synthesis of Substituted Benzoxazinones

Ajay Verma and Sangit Kumar*

Department of Chemistry, IISER Bhopal, Bhopal By-pass Road, Bhauri, Bhopal, Madhya Pradesh, 462066, India

Supporting Information

ABSTRACT: A transition metal (TM)-free practical synthesis of biologically relevant benzoxazinones has been established via a selective oxidative decarbonylative cleavage of an unstrained C(sp^3)–C(sp^2) bond employing iodine, sodium bicarbonate, and ^{t}butyl hydroperoxide in DMSO at 95 °C. Control experiments and Density Functional Theory (DFT) calculations suggest that the reaction involves a [1,5]H shift and extrusion of CO gas as the key steps. The extrusion of CO has also been established using PMA–$PdCl_2$.



Development of environmentally transcendent, operationally simple, and efficient strategies for the construction of privileged molecular skeletons continues to attract broad interest.[1] Transition metal (TM)-free reactions have attracted considerable attention from researchers because such methodologies avoid expensive and limited feedstocks of metals. Further, the removal of toxic heavy metals from the relevant drug molecules is challenging.[2] However, selectivity is one of the issues in TM-free reactions, particularly; the cleavage of unstrained C–C bonds has been a critical issue due to its uncontrollable selectivity and needed attention. Iodine[3] and peroxide[4] mediated reactions are the alternatives for the selective cleavage of C–C bonds for the synthesis of various heterocyclic molecules. Extensive research has been carried out for the cleavage of strained C–C bonds;[5] nonetheless, only a few reports are available for the selective cleavage of C(sp^3)–C(sp^2) bonds for the C–O bond formation.[6]

The benzoxazinone core is found in many drug molecules which possess various biological activities, namely serine protease inhibitor, antiobesity, inhibitors of human leukocyte elastase, and suicide inactivation of chymotrypsin inactivators (Figure 1).[7] Moreover, these moieties are intermediates for the synthesis of various molecules such as benzoxazinethiones, benzothiazinethiones, substituted amidobenzoates, 4-hydroxyquinolinones, and quinazolinones.[8] Various methods have been developed for the synthesis of benzoxazinones by organic and medicinal chemists which involved the TM-catalyst and carbon monoxide gas,[9] halogenated substrates,[10,11] and anhydrides.[12]

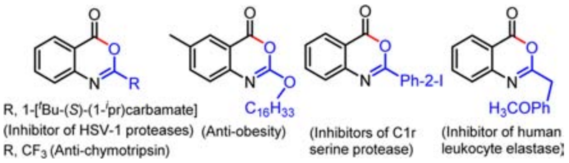
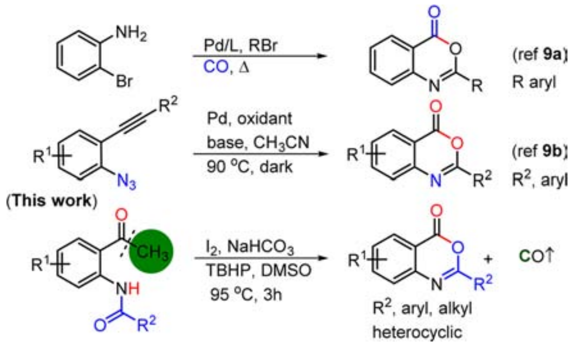


Figure 1. Biologically active substituted benzoxazinones.

Beller et al. described a Pd-catalyzed carbonylative synthesis of benzoxazinones from 2-bromoanilines using carbon monoxide (Scheme 1).[9a] Recently, the formation of benzoxazinones has been realized from azidoalkynes and CO gas, catalyzed by palladium(II) nitrate hydrate. Nonetheless, synthesis of the substrates involves multiple steps.[9b] Moreover, there is a lack of synthesis of substituted benzoxazinones from unactivated and halogen-free readily accessible substrates under mild reaction conditions. TM-free cleavage of a C–C bond has been accomplished in various substrates.[3f,6a,f] Nonetheless, the formation of CO has not been established. In continuation of our work[13] on TM-free synthesis via C–C[13a] and C–X (X = N, S, Se, Te)[13b–d] oxidative coupling reactions, herein, we disclose a practical synthetic method for the synthesis of substituted benzoxazinones from readily accessible *N*-(2-acetylphenyl)aryl/alkylamides **1** by the selective oxidative cleavage of an unstrained C(sp^3)–C(sp^2) bond using iodine and TBHP under mild reaction conditions.

Scheme 1. Synthetic Routes to Benzoxazinones



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Synthesis of benzoxazinone **2a** from *N*-(2-acetylphenyl)-2-methylbenzamide **1a** was optimized by screening various bases and oxidants in different solvents at different temperatures (Table 1). Initially, we applied iodine promoted C−N coupling reaction conditions (entry 1);[13b] unfortunately, none of the expected products **2a**, **3**, and **4** was observed, and substrate **1a** was recovered from the reaction mixture. Among various screened oxidants (entries 2−6), DTBP, aq. H_2O_2, and $M_2S_2O_8$ (M = Na and K) failed to facilitate the decarbonylative coupling reaction. $PhI(OAc)_2$ and aqueous TBHP provided benzoxazinone **2a** in 15% and 26% yields along with undesired aldol 2-(*o*-tolyl)quinolin-4(1*H*)-one **3** in 60% and 54% yields, respectively (entries 5 and 6). Anhydrous TBHP led to further improvement in the yield by 46%; however, 2-phenylquinolin-4(1*H*)-one **3** was also formed albeit in low yield (entry 7). Among various bases (entries 8−11), $NaHCO_3$ was found to be superior. Potassium *tert*-butoxide along with iodine, which could form iodide and ^{t}butoxyl radicals, also failed to yield any **2a**, and instead **3** was obtained exclusively (entry 12). The use of 50 mol % of iodine together with $NaHCO_3$ provided exclusive formation of **2a** (entry 13). Further reduction in the iodine loading to 20 mol % was not effective as this provided **2a** in low yield (70%) and also undesired **3** in 20% yield (entry 14). Worth noting, a base, iodine, and TBHP are crucial for the reaction, as the absence of any one of them failed to yield benzoxazinone **2a**. The temperature ranging from 90 to 100 °C was noted to be optimum for the reaction. An excess of anhydrous TBHP seems necessary for the quantitative yield of benzoxazinone **2a** (entry 13 vs 15).

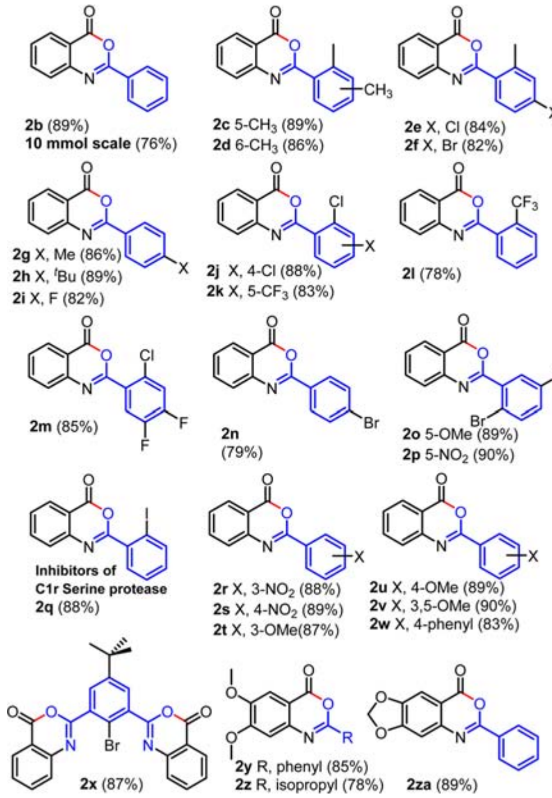
Table 1. Optimization of Reaction Conditions[a]

entry	bases	oxidants	temp	yield, 2a/3
1[b]	K_2CO_3	DTBP	140	0/0
2	$NaHCO_3$	H_2O_2(aq)	95	nd
3	$NaHCO_3$	$Na_2S_2O_8$	95	nd
4	$NaHCO_3$	$K_2S_2O_8$	95	nd
5	$NaHCO_3$	$PhI(OAc)_2$	95	15/60
6	$NaHCO_3$	TBHP(aq)	95	26/54
7[b]	K_2CO_3	TBHP	95	72/10
8[b]	K_2CO_3	–	95	nd/trace
9[b]	K_2CO_3	TBHP	95	69/10
10[c]	K_2CO_3	–	95	nd/60
11[c]	KO^{t}Bu	–	95	nd/80
12	KO^{t}Bu	–	95	nd/70
13	**$NaHCO_3$**	**TBHP**	**95**	**93/0**
14[d]	$NaHCO_3$	TBHP	95	70/20
15	$NaHCO_3$	TBHP (3 equiv)	95	55/10

[a]Reactions were carried out with 0.16 mmol of **1a**, 0.08 mmol of I_2, 0.16 mmol of a base, and 0.96 mmol of oxidant in 1.5 mL of anhydrous DMSO. [b]2 equiv of I_2 was used. [c]Absence of I_2. [d]0.2 equiv of I_2 was used. nd = not detected.

With the optimized conditions in hand, a variety of *N*-(2-acetylphenyl)-2-methylbenzamide substrates **1b**−**1za** were explored for decarbonylative coupling between acetyl and amide moieties. As shown in Scheme 2, various benzamide ring substituted benzoxazinones **2b**−**2za** with electron-donating methyl, *tert*-butyl, methoxy, and dimethoxy as well as electron-withdrawing halogens, CF_3, and nitro at different positions of the benzamide ring were obtained without a significant difference in the isolated yields. Benzoxazinone **2b** has also been synthesized practically in gram quantity in overall 76% yield. *ortho*-Iodo-substituted benzoxazinone **2q** possessing C1r protease inhibition activity[7c] was synthesized in 88% yield under the decarbonylative coupling reaction. Similarly, biologically relevant biaryl benzoxazinone **2w** was obtained. Further, molecule **2x** with a bis-benzoxazinones moiety, which could be used as a ligand for various metals complexation,[14] has been isolated in 87% yield. Substitution in the benzamide ring of 2′-aminoacetophenones with dimethoxy, dioxole groups also proceeded in the decarbonylative C−O coupling reaction to generate electron-rich benzoxazinones **2y**−**2za** in 78−89% yields. Structures of benzoxazinones **2i** and **2p** are well established by single crystal X-ray crystallography (Figure 2).[15]

Scheme 2. Substrate Scope for 2-Aryl Benzoxazinones[a]



[a]Reactions were carried out using 0.3 mmol of **1**, 0.15 mmol of I_2, 0.3 mmol of $NaHCO_3$, and 1.8 mmol of TBHP in DMSO.

Next, heterocyclic amides namely 2-furan as well as 2- and 3-thiophenes successfully underwent the TM-free decarbonylative coupling reaction and resulted in heterocyclic benzoxazinones **5a**−**5c** in 88−90% yields (Figure 3). Similarly, *primary*, *secondary*, and *tert*-alkyl amides smoothly experienced decarbon-

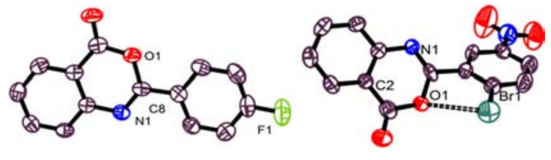


Figure 2. ORTEP diagrams of benzoxazinone **2i** and **2p**.

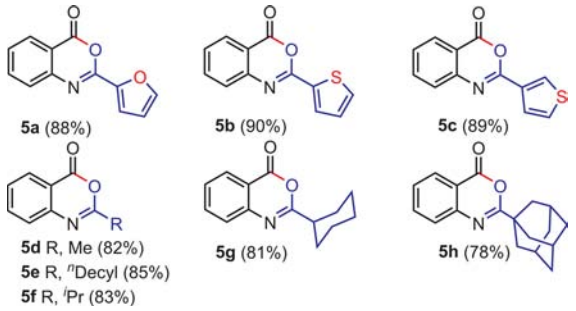
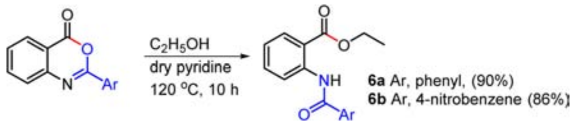


Figure 3. Substrate scope for heteroaryl/alkyl benzoxazinones.

ylation followed by a C−O coupling reaction to form 2-alkyl-4*H*-benzo[*d*][1,3]oxazin-4-ones **5d**−**5h**.

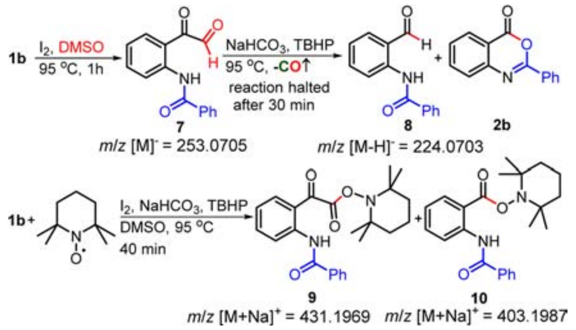
Further, synthesized benzoxazinones have been functionalized to ethyl-2-arylamidobenzoate **6a** and **6b** in 90% and 86% yield, respectively, using ethanol and pyridine (1:1) in a sealed tube at 120 °C for 10 h (Scheme 3). Benzoxazinones can also be transformed into biologically imperative quinazolinones.[8]

Scheme 3. Postsynthetic Modification



Mechanistic insights are gained by conducting several control experiments, and DFT calculations (Scheme 4). Reaction of *N*-(2-acetylphenyl)benzamide **1b** with iodine in DMSO gave 2-oxoacetyl intermediate **7**.[16] Subsequently, the addition of TBHP and $NaHCO_3$ to *in situ* formed **7** provided benzaldehyde **8** and benzoxazinone **2b** by an evolution of CO gas. The addition of TEMPO to the reaction mixture yielded TEMPO-coupled products **9** and **10** along with benzoxazinone **2b** as analyzed by high-resolution mass spectrometry (see Supporting Information pp S30−S34).

Scheme 4. Characterization of Intermediates by ES-MS



Evolution of CO gas from the reaction mixture was confirmed by phosphomolybdic acid (PMA)−$PdCl_2$ solution (Figure 4 and a short movie is attached to SI p S29). PMA $[H_3PO_4(Mo^{VI}O_3)_{12}]$ oxidizes evolved CO gas into CO_2 in the presence of catalyst $PdCl_2$, and yellow PMA reduced into a blue-green colored mixed-valence heteropolymolybdate complex (Mo^{VI} Mo^{V}).[17] The generated CO gas can be exploited in the synthesis of various natural products via a carbonylation reaction.[18]

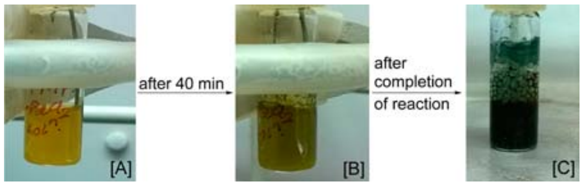
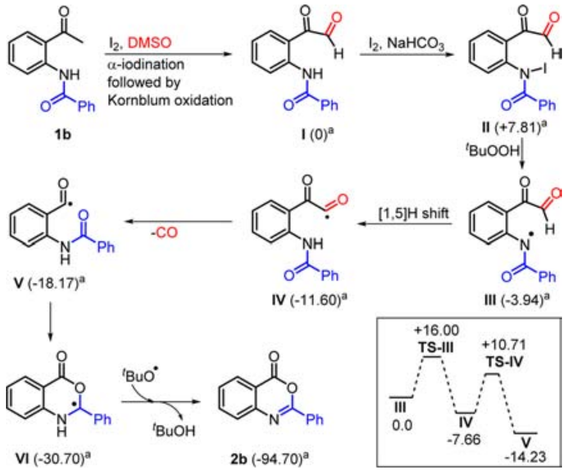


Figure 4. Qualitative analysis for the extrusion of CO gas.

Based on control experiments, a plausible mechanism for the decarbonylative reaction is depicted in Scheme 5. *N*-(2-Acetylphenyl)benzamide undergoes *α*-iodination followed by Kornblum oxidation that led to 2-oxoacetyl intermediate **I**.[16b]

Scheme 5. Plausible Reaction Mechanism



[a]Calculated relative Gibbs' free energy (ΔG° in kcal mol^{-1}) obtained at the DFT-B3LYP/6-311+G(d,p)/CPCM, (LanL2DZ for iodine) level of theory. Energy barrier of key steps (**III**−**V**).

The generated HI in the step oxidized to molecular iodine by DMSO (see SI p S30). The resulting 2-oxoacetyl **I** could react with iodine in the presence of $NaHCO_3$ to give *N*-iodo-oxoacetyl **II**. The presence of $NaHCO_3$ seems crucial to this transformation, as in its absence benzoxazinone cannot be realized. *N*-Iodo-oxoacetyl **II** would produce amidyl radical **III** in the presence of TBHP.[13b] Translocation of the radical to the carbonyl carbon by a [1,5]H shift should furnish carbon-centered radical **IV**, which transforms to another carbon-centered radical **V** by CO elimination. An intramolecular transfer of the radical to the amidic carbonyl carbon would provide cyclized radical **VI**. The abstraction of a hydrogen atom by a ^{t}butoxy radical or the *N*-iodo-oxoacetyl **II** intermediate would furnish the desired benzoxazinone.

Additionally, we complemented the proposed mechanism with DFT computations, to study key intermediates and transition states involved in the reaction in DMSO solvent (see SI p S35−47). The negative Gibbs free energy changes for **III**−**VI** except **II** are indicative of the thermodynamic feasibility of the reaction (Scheme 5). The [1,5]H-shift and evolution of CO gas seem to be crucial steps in the transformation and could occur through transition states **TS-III** and **TS-IV**, respectively. The energies barriers ($\Delta G^{\#}$) for these steps are +16.00 and +10.71 kcal mol^{-1}, respectively, which could be achievable under the reaction conditions.[3k]

In summary, we have presented a practical synthetic method for the preparation of diversely substituted benzoxazinones from *N*-(2-acetylphenyl)benzamide via oxidative decarbonylative cleavage of an unstrained $C(sp^3)-C(sp^2)$ bond avoiding prefunctionalized or halogenated substrates, TM-catalysts, and harsh reaction conditions. The [1,5]H shift and extrusion of CO gas are crucial steps in the oxidative decarbonylative cleavage of the unstrained C(sp^3)−C(sp^2) bond. Further understanding of the reaction and oxidative coupling in another class of amines is currently being pursued in our laboratory.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b02142.

Experimental details, spectroscopic data, mass spectra (PDF)

X-ray crystallographic data for **2i** [CCDC No. 1474945] (CIF)

X-ray crystallographic data for **2p** [CCDC No. 1474944] (CIF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: sangitkumar@iiserb.ac.in.

Notes

The authors declare no competing financial interest.

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(15) **2i** is observed as planar molecule and **2p** crystallized in a chiral space group $P2_12_12_1$ with a good Flack parameter value of 0.028(11) (see SI pp S49−S61). The strong intramolecular Br···O interaction [Br + O = 3.027(4) Å] seems to be responsible for the crystallization of the single enantiomorph.

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