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Tetrahedron Letters

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Palladium-catalyzed *ortho*-acylation of N-Nitrosoanilines with α -oxocarboxylic acids: a convenient method to synthesize N-Nitroso ketones and indazoles

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ARTICLE INFO

Article history:

Received 19 March 2016

Revised 24 April 2016

Accepted 26 April 2016

Available online 27 April 2016

ABSTRACT

An efficient and mild protocol for regioselective synthesis of N-Nitroso aryl ketones by palladium-catalyzed direct acylation of arenes using N-Nitroso as directing groups is described. This reaction proceeded smoothly and could tolerate a variety of functional groups. Moreover, this chemistry offers a convenient access to a range of indazoles.

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Keywords:

Palladium-catalyzed

Acylation

C–H bond cleavage

N-nitroso ketones

Indazoles

Transition metal catalyzed C–H functionalization is an atom- and step-economical approach for the rapid construction of carbon–carbon or carbon–heteroatom bonds.^{1,2} It has been utilized in the synthesis of various organic molecules. Most of the established site-selective C–H activations depend on directing groups that can coordinate to metal catalysts therefore assist the regioselective transformations.³ Indeed, the coordinating groups such as pyridyl,⁴ acetyl,⁵ acetamino,⁶ carboxylic acid,⁷ nitriles,⁸ azo,⁹ ketones,¹⁰ and oxazolyl¹¹ for regio- and chemoselective C–H bond cleavage have been extensively investigated. Although a number of methods have been developed, novel directing groups and effective catalytic systems are still highly desirable for expanding the realm of selective C–H functionalization. To the best of our knowledge, N-Nitroso compounds, which have been recently proved to be an efficient traceless directing group,¹² have rarely been studied due to the fragile nitrogen–nitrogen bond which can be easily cleaved under reaction conditions applied.^{12,13}

Aromatic ketone is an important structural motif in pharmaceuticals and natural products¹⁴ and it can be prepared via numerous established methods. Compared with the traditional methods of Friedel–Crafts acylation relying mainly on Lewis acids or Bronsted

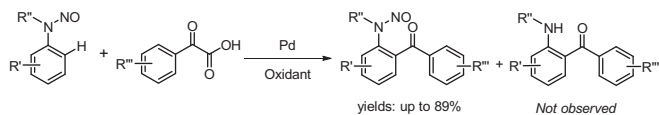
acids¹⁵ and various oxidants,¹⁶ the emergence of direct functionalization of the inert C–H bond is considered to be an efficient strategy in recent years due to the advantage of atom-economy and step-economy with no preactivation of arenes and minimization of wasteful byproducts.¹⁷ More importantly, N-Nitroso ketones, which are a class of very useful medicinal compounds with nitrogen containing ketones,¹⁸ have not received much attention from the synthetic community due to limited supply of *ortho*-aminobenzophenones. Although significant progress for the *ortho*-selective functionalization of N-Nitrosoanilines has been achieved,^{12,13} there is no report on the direct synthesis of N-Nitroso ketones,¹⁹ which represent profoundly more desirable target as synthetically highly important yet unmet goal. In continuation of our previous work on C–H functionalization of azoxy compounds,²⁰ herein, we describe a novel efficient approach for accessing a number of different N-Nitroso ketones by Pd-catalyzed *ortho*-C–H bond acylation with various commercially accessible or easily prepared N-Nitrosoanilines (Scheme 1).²¹

To probe the feasibility of this approach, we initiated our studies with N-methyl-N-Nitrosoaniline (**1a**, 1.0 equiv) and α -oxocarboxylic acids²² (**2a**, 2.0 equiv) with K₂S₂O₈ (2.0 equiv) in the presence of 10 mol % Pd(OAc)₂ in Dioxane at 80 °C for 20 h. To our delight, the desired product **3aa** was isolated in 65% yield, and possible byproduct that could be derived from N–NO bond cleavage is not observed (Table 1, entry 1). Encouraged by this

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Scheme 1. Site-selective *ortho*-acylation of Nitrosoanilines.

result, the effect of solvents on this transformation was examined, and Diglyme proved to be crucial (Table 1, entry 1–7). It was found that $K_2S_2O_8$ was superior to other oxidants including $(NH_4)_2S_2O_8$, $Na_2S_2O_8$, and Oxone, affording the desired N-Nitroso ketone **3aa** in 83% isolated yield, while other oxidants such as BQ and AgOAc were not effective and no N-Nitroso ketone product was isolated from those attempts (Table 1, entry 8–12). Further catalyst screening showed that a noticeable (6%) increase in yield was observed when $Pd(TFA)_2$ was involved in the reaction, and the corresponding product was achieved in 89% yield (Table 1, entry 15).²³ Additionally, no reaction took place in the absence of a palladium catalyst even at high temperatures and longer reaction times (Table 1, entry 16). It should be noted that increasing the loading of catalyst could not enhance the yield of the corresponding ketone obviously, while lowering the amount of $Pd(TFA)_2$ to 5 mol % suppressed the efficiency (Table 1, entry 17). Moreover, changing the reaction temperature and reducing the stoichiometry of oxidant did not favor the acylation progress (Table 1, entry 18–20). In summary, the optimized reaction conditions for the *ortho*-C–H acylation of N-Nitroso compounds were obtained as follows: 10 mol % $Pd(TFA)_2$ as the catalyst, 2.0 equiv of $K_2S_2O_8$ as the oxidant, and Diglyme as the solvent, at 80 °C under argon for 20 h.

Table 1
Optimization of the reaction conditions^a

Entry	Catalyst	Oxidant	Solvent	Yield ^b (%)
1	$Pd(OAc)_2$	$K_2S_2O_8$	Dioxane	65
2	$Pd(OAc)_2$	$K_2S_2O_8$	DCE	56
3	$Pd(OAc)_2$	$K_2S_2O_8$	Toluene	63
4	$Pd(OAc)_2$	$K_2S_2O_8$	DME	68
5	$Pd(OAc)_2$	$K_2S_2O_8$	DMSO	0
6	$Pd(OAc)_2$	$K_2S_2O_8$	CH_3CN	40
7	$Pd(OAc)_2$	$K_2S_2O_8$	Diglyme	83
8	$Pd(OAc)_2$	$(NH_4)_2S_2O_8$	Diglyme	66
9	$Pd(OAc)_2$	$Na_2S_2O_8$	Diglyme	41
10	$Pd(OAc)_2$	Oxone	Diglyme	34
11	$Pd(OAc)_2$	Ag_2CO_3	Diglyme	0
12	$Pd(OAc)_2$	BQ	Diglyme	0
13	$PdCl_2$	$K_2S_2O_8$	Diglyme	30
14	$PdCl_2(MeCN)_2$	$K_2S_2O_8$	Diglyme	10
15	$Pd(TFA)_2$	$K_2S_2O_8$	Diglyme	89
16	$Pd(TFA)_2$	$K_2S_2O_8$	Diglyme	0
17 ^c	$Pd(TFA)_2$	$K_2S_2O_8$	Diglyme	77
18 ^d	$Pd(TFA)_2$	$K_2S_2O_8$	Diglyme	74
19 ^e	$Pd(TFA)_2$	$K_2S_2O_8$	Diglyme	66
20 ^f	$Pd(TFA)_2$	$K_2S_2O_8$	Diglyme	58
21 ^g	$Pd(TFA)_2$	$K_2S_2O_8$	Diglyme	76

^a All the reactions were carried out in the presence of 0.2 mmol of **1a**, 0.4 mmol of **2a**, and 0.4 mmol of oxidants in 1.0 mL of solvents at 80 °C for 20 h under Ar.

^b Isolated yields.

^c 5 mol % $Pd(TFA)_2$ was used.

^d 1.5 equiv of $K_2S_2O_8$ was used.

^e At 100 °C.

^f At 60 °C.

^g Under air condition.

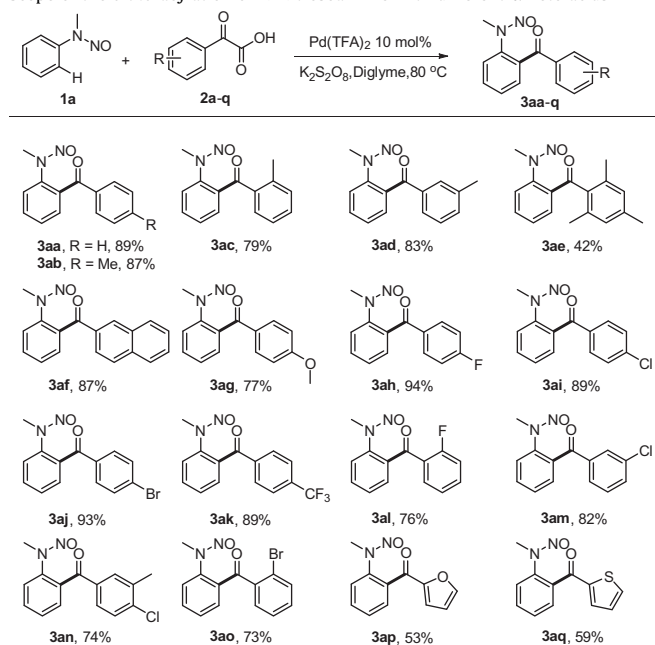
Under the established reaction conditions, the scope of the Pd-catalyzed *ortho*-acylation of N-methyl-N-Nitrosoaniline with α -oxocarboxylic acids was investigated (Table 2). The coupling of benzoylformic acids with electron-donating and withdrawing groups at the phenyl ring all underwent the intended transformation smoothly and good to excellent yields were obtained in most cases. The substitution on the aromatic ring of benzoylformic acids demonstrated that no significant electronic effect was present. For example, the substrates with an electron donation methyl group and methoxyl group afforded the desired N-Nitroso ketones in good yields, while electron-withdrawing group-substitute on phenyl ring, such as F, Cl, Br, and CF_3 provided comparative results. It is worth noting that this chemistry was sensitive to the steric hindrance when *ortho*-disubstituted benzoylformic acid was involved in the reaction, and the corresponding ketone was isolated in 42% yields (**3ae**). It's worth noticing that, the chloro and bromo groups remained intact in this procedure with good yields (**3ai–3aj**, **3am–3ao**), which offer versatile synthetic functionality for further transformations into other significant structures. Much to our pleasure, this transformation can also be successfully extended to heterocyclic-substituted α -keto acids with moderate yields (**3ap–3aq**), which proved a broad range of substrates in this highly effective process.

We next examined the scope of different N-Nitroso compounds with α -oxocarboxylic acids under our best conditions (Table 3). It was found that this transformation also showed good tolerance toward the N-Nitrosoaniline with either electron-rich or electron-deficient groups, and various halogen groups are tolerated, for example F (**3fa**), Cl (**3ga**), and Br (**3ha**) groups, utilizing as the handle for further functionalization. Notably, a strong electron donating group (OMe) at the *para*-position of aromatic ring of N-Nitroso compounds furnished **3ea** in a relatively lower yield with some unidentified by-products, while a *para*-trifluoromethyl substituted N-methyl-N-Nitrosoarylamine also provided moderated yield, probably due to its low reactivity. As expected, the N-ethyl-N-Nitroso ketone and N-isopropyl-N-Nitroso ketone can also be obtained by this protocol, although both *cis* and *trans* isomers were obtained in the products due to the restricted rotation around the N-Nitroso N–N bond.

A possible pathway was proposed to account for this *ortho*-acylation of N-Nitroso compounds, which was described in Scheme 2.^{12,13,22} N is generally considered to be a better coordinating atom than O. It is believed that this transformation is probably initiated by N-assisted *ortho*-palladation on the arene ring by Pd(TFA)₂, providing the highly reactive palladacycle **I**,²³ followed by reaction with α -keto acid to afford cyclopalladated complex **II** along with release of CF_3COOH . Subsequently, the obtained active complex **II** underwent a decarboxylation procedure to form complex **III**,²⁴ which further underwent reductive elimination to afford the corresponding acylated product **3aa** and Pd(0). Finally, the generated Pd(0) catalyst can be reoxidized to the active Pd(II) catalyst in the presence of $K_2S_2O_8$.

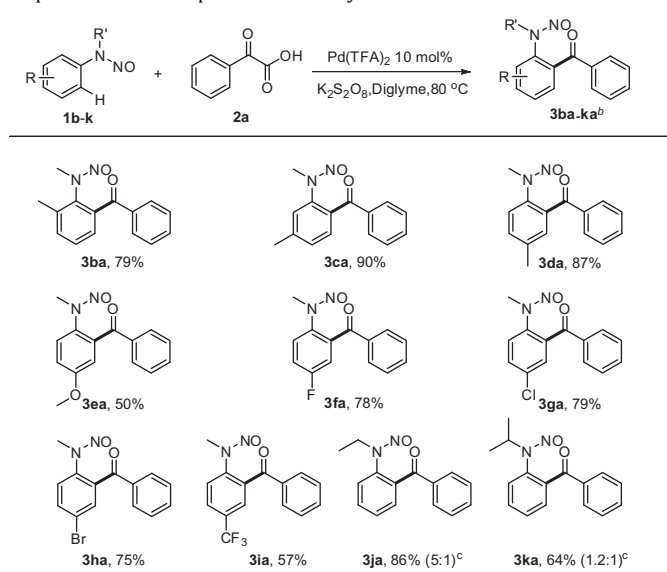
To demonstrate the synthetic utility of this method, the further transformation of the acylated N-Nitrosoanilines into 3-aryl-indazoles was examined. Albeit their scarcity in nature, 3-aryl-indazole is an important class of heterocycles that is being evaluated in medicinal and agrochemical research.²⁵ Previously reported synthesis of these compounds involves harsh reagents (e.g., explosive or toxic reagents, expensive catalysts) therefore they are less than satisfactory.²⁶ Much to our pleasure, when the commercially available Zn powder was used to reduce N-Nitroso ketones in AcOH at room temperature, the transformation of acylated N-Nitrosoaniline into 3-substituted indazoles was completed in 24 h with nearly quantitative yields (Table 4).

In summary, we have developed a novel catalytic system for Pd-catalyzed decarboxylative *ortho*-acylation of N-Nitroso compounds

Table 2Scope of the *ortho*-acylation of N-Nitrosoaniline with different α -keto acids^{a,b}

^a All the reactions were carried out in the presence of 0.2 mmol of **1a**, 0.4 mmol of **2**, and 0.4 mmol of K₂S₂O₈ in 1.0 mL of Diglyme at 80 °C for 20 h under Ar.

^b Isolated yields.

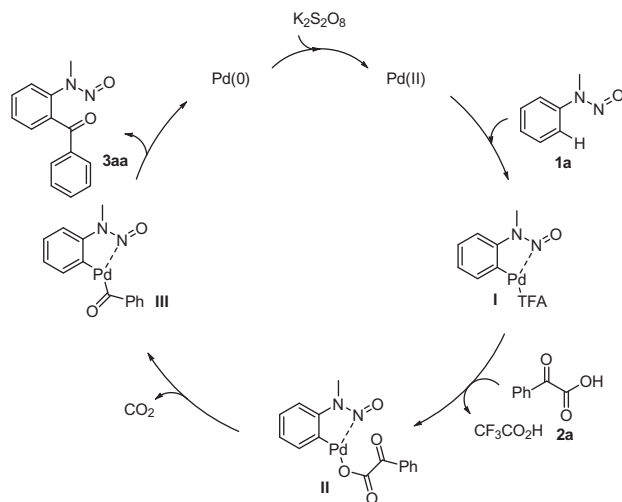
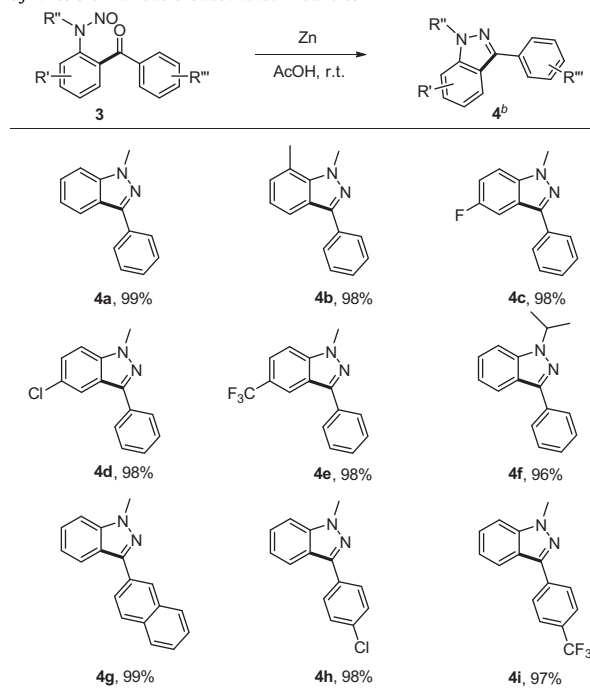
Table 3Scope of N-Nitroso compounds in *ortho*-acylation reactions^{a,b}

^a All the reactions were carried out in the presence of 0.2 mmol of **1**, 0.4 mmol of **2a**, and 0.4 mmol of K₂S₂O₈ in 1.0 mL of Diglyme at 80 °C for 20 h under Ar.

^b Isolated yields.

^c The ratio of the *syn* to *anti* isomers relative to N–N bond, determined by the ¹H NMR spectra.

with α -oxocarboxylic acids via N atom-directed activation of C–H bond to synthesis of N-Nitroso ketones, which could be further transformed into various 3-substituted indazoles. This simple methodology employing available N-Nitrosoanilines, the extensive scope observed and easily transformation is very attractive to synthetic chemists. Ongoing research of our group is focused on applying this new methodology in synthesis and exploring other

**Scheme 2.** Proposed reaction mechanisms.**Table 4**Synthesis of various 3-substituted indazoles^{a,b}

^a All the reactions were carried out in the presence of 0.25 mmol of **3**, 1.25 mmol of Zn powder in 1.0 mL of AcOH at room temperature for 24 h.

^b Isolated yields.

potential reaction partners with N-Nitroso anilines besides oxocarboxylic acid. Acylation of sp³ C–H bond is also under investigation in our lab.

Acknowledgments

We are grateful to the Northwest University (NF14020), Shaanxi Provincial Science and Technology Development Funds (2016JQ2022), the National Natural Science Foundation of China (21402071), and National Found for Fostering Talents of Basic Science (NFFTBS-J1103311, J1210057) for financial support.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.tetlet.2016.04.096>.

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