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Pd-Catalyzed Multidehydrogenative Cross-Coupling between (Hetero)Arenes and Nitroethane to Construct β-Aryl Nitroethylenes

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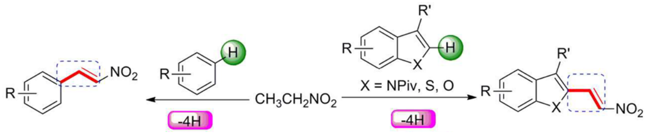
ABSTRACT



The Pd-catalyzed multidehydrogenative cross-coupling reactions of arenes with nitroethane are described. The established methods afford β-aryl nitroethylenes that are an important class of synthetic intermediates and biologically active compounds in an atom- and step-economical fashion. The reactions were applicable to substituted benzenes and a variety of heterocycles such as benzothiophenes, benzofurans, and indoles. Mechanistic experiments indicated that β-nitroethylbenzene might be the intermediate in this transformation.

β-Aryl nitroethylenes and the compounds with β-aryl nitroethylene structural units are versatile intermediates in organic syntheses owing to various transformations of such structural units,[1] such as selective reductions to diverse functional groups,[2] the Diels–Alder cycloaddition reactions,[3] and the Michael addition reactions to construct carbon–carbon or carbon–heteroatom bonds.[4] Yet, many β-aryl nitroethylenes and their derivatives have been documented to display diverse biological activities including antibacterial, molluscicidal,[5] and anticancer.[6]

The most commonly used method for the preparation of β-aryl nitroethylenes is the Henry condensation reaction of aromatic aldehydes with nitromethane,[7] which is usually carried out under basic conditions (Scheme 1). Given that aromatic aldehydes are generally prepared from the corresponding arenes by way of the Gattermann–Koch formylation[8] or the Vilsmeier–Haack formylation[9] process, a significant improvement would be made if β-aryl nitroethylenes could be directly synthesized from arenes. Herein, we

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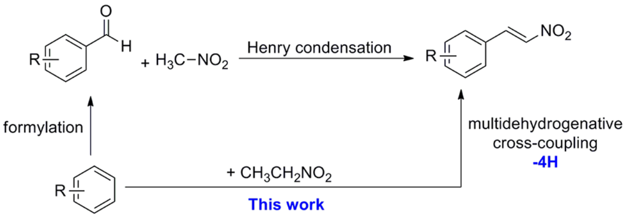
demonstrate that this goal could be achieved through Pd-catalyzed cross-coupling reactions of (hetero)arenes with nitroethane via 4-fold C–H bond cleavages.

Scheme 1. Methods for Construction of β-Aryl Nitroethylene



In the past few years, substantial progress has been achieved in the development of catalytic methods for the dehydrogenative cross-coupling between two C_{sp^2}–H bonds[10,11] or between a C_{sp^2}–H bond and a C_{sp^3}–H bond adjacent to heteroatoms or aromatic rings.[12] Recently, when investigating the decarboxylative cross-couplings of arene carboxylic acids with saturated ketones or nitroethane,[13] we found that they afforded the decarboxylative Heck-type products. On the basis of these findings, we have developed the Pd-catalyzed multidehydrogenative cross-coupling of (hetero)arenes and the saturated ketones.[14] To expand such a new type of multidehydrogenative cross-coupling further, we considered whether the reaction of (hetero)arenes with nitroethane under a Pd catalyst affords β-aryl nitroethylenes. The expected tandem transformation, which just involves multiple successive C–H cleavages and C–C formation steps in one pot,[15] would provide a fundamentally new approach that enables the facile synthesis of β-aryl nitroethylenes in an atom- and step-economical fashion. However, achievement of this target reaction remains a great challenge because the successive cleavage of the C–H bond and the formation of the C–C bond would be required in this process.

Taking into account the above problems, we screened a variety of reaction parameters by reacting mesitylene (**1a**, 1 mL) with nitroethane **2** as a model system (Table 1). The desired product **3a** was obtained in 7% yield from the reaction carried out in DMSO/DME (DME = 1,2-dimethoxyethane) at 100 °C with 10 mol % $Pd(TFA)_2$ as a catalyst and Ag_2CO_3 (2.0 equiv) as an oxidant (entry 2). In the previous studies on the dehydrogenative cross-coupling reactions involving the dehydrogenation of saturated ketones to olefins,[13b,14] we observed that additional bases were required to promote the olefin formation from saturated ketones and accept the protons from the reaction. However, the additional bases such as carboxylate salts and carbonates totally shut down the reaction of **1a** with **2**, probably because these bases competed for coordination to the Pd center preferentially over substituted benzene or a reaction intermediate and therefore impeded the desired catalytic process (entries 5–7). In line with this speculation, weakly polar ethers provided better results than strongly polar solvents such as DMA and NMP (entries 13–16). Nevertheless, control experiments showed that 35–70 equiv of DMSO were indispensable for this reaction to occur (entry 8). These observations suggested that a Pd complex with DMSO as the ligand may be involved in the catalytic process.[16] The use of AgOAc (4.0 equiv) to replace Ag_2CO_3 significantly improved the yield (entries 3–4). Other silver salts such as AgTFA, Ag_2O, and AgOTf were observed to be inferior to AgOAc. The beneficial effect of AgOAc may arise from either the liberation of acetate anion at a suitable rate through the reduction of AgOAc or the formation of a reactive catalyst from $Pd(TFA)_2$ and AgOAc.[11b] Other commonly used oxidants for the oxidation of Pd(0) to Pd(II) such as BQ, $Cu(OAc)_2$, and O_2 were totally invalid (entries 10–12). Interestingly, the reaction could be carried out under air without a loss in yield (entry 17).

With the optimized reaction conditions in hand (10 mol % $Pd(TFA)_2$, 4.0 equiv of AgOAc in DMSO/

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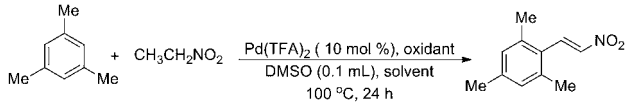
Table 1. Optimization Studies of Reaction Conditions[a]



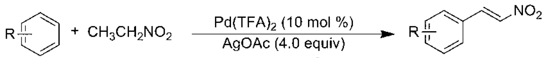
1a (excess) **2** **3**

entry	**1a** (mL)	oxidant/additive (equiv)	solvent	yield (%)[b]
1	0.5	Ag_2CO_3 (2.0)	DME	trace
2	1.0	Ag_2CO_3 (2.0)	DME	7
3	0.2	AgOAc (4.0)	DME	20
4	0.5	AgOAc (4.0)	DME	75 (81)
5	0.5	AgOAc (4.0)/ LiOAc (20 mol %)	DME	7
6	0.5	AgOAc (4.0)/ K_2CO_3 (20 mol %)	DME	0
7	0.5	AgOAc (4.0)/ PivOk (20 mol %)	DME	3
8[c]	0.5	AgOAc (4.0)	DME	6
9	0.5	AgTFA (4.0)	DME	trace
10	0.5	BQ (2.0)	DME	0
11	0.5	$Cu(OAc)_2$ (2.0)	DME	0
12	0.5	O_2 (1 atm)	DME	0
13	0.5	AgOAc (4.0)	DEE	69
14	0.5	AgOAc (4.0)	dioxane	73
15	0.5	AgOAc (4.0)	DMA	23
16	0.5	AgOAc (4.0)	NMP	18
17[d]	0.5	AgOAc (4.0)	DME	72

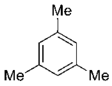
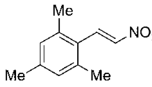
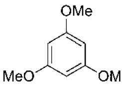
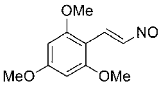
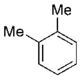
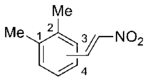
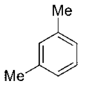
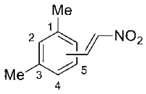
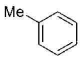
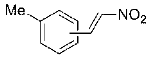
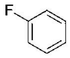
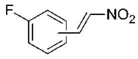
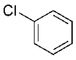
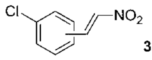
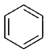
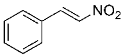
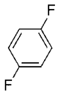
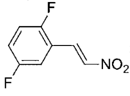
[a] Reaction conditions: mesitylene **1a** (excess), nitroethane **2** (0.2 mmol), $Pd(TFA)_2$ (10 mol %), oxidant, DMSO (0.1 mL), solvent (0.5 mL), 100 °C, 24 h. [b] GC yields with dodecane as internal standard (values in parentheses refers to the isolated yield). [c] In absence of DMSO. [d] Under air. DEE = 1,2-diethyoxylethane. DMA = *N*,*N*-dimethylacetamide. NMP = *N*-methyl-2-pyrrolidone.

DME, 100 °C, 24 h), we next evaluated the scope of substituted benzenes. As depicted in Table 2, an array of substituted benzenes smoothly underwent the reaction with nitroethane to produce substituted β-aryl nitroethylenes exclusively. Since the size of nitroethane is relatively small, the reactivity and regioselectivity of the reactions were predominantly governed by the electronic effect of the substituents rather than steric hindrance. Electron-rich arenes such as 1,3,5-trimethoxybenzene, even though sterically encumbered, provided the desired product in good yield (**3b**), while benzene, toluene, and xylene underwent the reaction in reduced yields (**3c**, **3d**, **3e**, **3h**). Note that only 3.0 equiv of electron-rich 1,3,5-trimethoxybenzene were required for a good yield. For *m*-xylene, the cross-coupling mainly occurred at the more electron-rich C2- and C4-position (**3d**). In the case of *o*-xylene, in which the two different aromatic C−H bonds are electronically similar but have different steric environments, the reaction preferred the less hindered C4-position over the C3-position (**3c**). The monosubstituted benzenes gave a mixture of *ortho*, *meta*, and *para* regioisomers (**3e**, **3f**, and **3g**), and the ratio of the three regioisomers depended on the nature of the substituents. Toluene and chlorobenzene offered the mixture with the *ortho* isomer slightly more than the other two, while the small fluoro substituent obviously favored the reaction at its adjacent C−H bond. 1,4-Difluorobenzene could also take part in this reaction to afford the corresponding product in a good yield (**3i**). Other electron-withdrawing substituents such as the ester, nitro, and cyano group were ineffective. When other nitroalkanes such as 1-nitropropane, 2-nitropropane, and nitrocyclohexane were induced to react with **1a** under the established conditions, the desired products were not obtained.

Table 2. Pd-Catalyzed Cross-Coupling of Simple Arenes with Nitroethane[a]



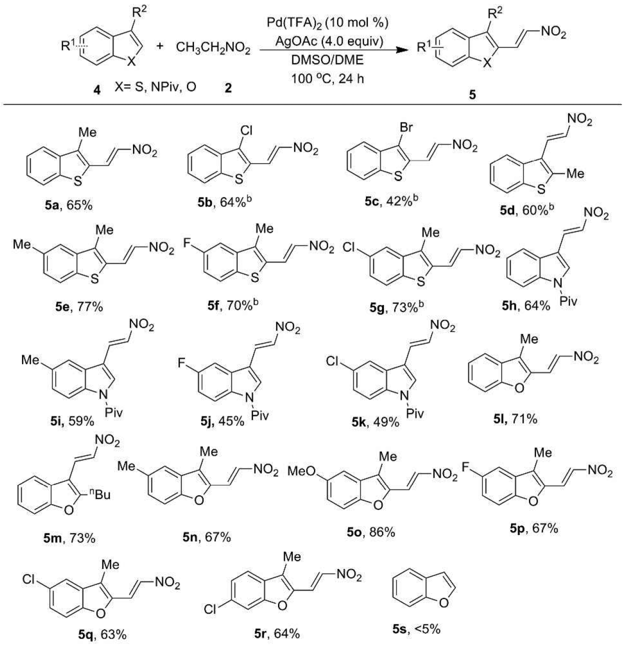
1 **2** **3**

entry	arene	product	yield[b]
1	 **1a**	 **3a**	81%
2	 **1b**	 **3b**	78%[c]
3	 **1c**	 **3c**	65% (1,2,3:1,2,4 = 1:2)
4	 **1d**	 **3d**	62% (1,2,3:1,3,4:1,3,5 = 2:5.8:1)[d]
5	 **1e**	 **3e**	52% (*o*:*m*:*p* = 1.4:1:1.1)
6	 **1f**	 **3f**	55% (*o*:*m*:*p* = 6.5:1:2)
7	 **1g**	 **3g**	47%[e] (*o*:*m*:*p* = 1.1:1:1)
8	 **1h**	 **3h**	50%[e]
9	 **1i**	 **3i**	68%[e]

[a] Reaction conditions: arene (0.5 mL), nitroethane (0.2 mmol), $Pd(TFA)_2$ (10 mol %), AgOAc (4.0 equiv), DMSO (0.1 mL), DME (0.5 mL), 100 °C, 24 h. [b] Isolated yield; the value given in parentheses denotes the relative ratio of isomers determined by GC-MS. [c] 1,3,5-Trimethoxybenzene (3.0 equiv). [d] The ratio of isomers was determined by ^1H NMR. [e] DMSO (0.05 mL).

Given that the electron-donating group shows a beneficial influence on the reactivity of substituted benzenes, we speculated that the electron-rich heteroarene **4** might also be suitable for the cross-coupling with nitroethane. We were pleased to found that, when the ratio of **4**/**2** reversed to 1:7 and the amount of solvent was increased to 2 mL, the reaction was also applicable to a range of substituted benzothiophenes, benzofurans, and indoles (Scheme 2). The variety of substituents tolerated in these cross-couplings, such as fluoro, chloro, bromo, methyl, and methoxyl, provide opportunities for further synthetic elaboration. Interestingly, in the cases of benzothiophenes and benzofurans, a substituent, at either the C2 or C3 position, was required to obtain good yields, of which the cause is under investigation (**5a**–**5g**, **5l**–**5s**).

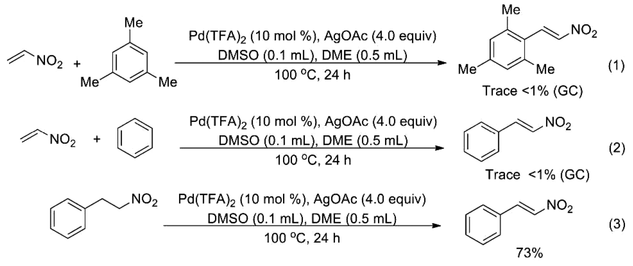
Scheme 2. Pd-Catalyzed Cross-Coupling of Aromatic Heterocycles with Nitroethane[a]



[a] Reaction conditions: heterocycles (0.2 mmol), nitroethane (7.0 equiv), Pd(TFA)$_2$ (10 mol %), AgOAc (4.0 equiv), DMSO (0.1 mL), DME (2.0 mL), 100 °C, 24 h. [b] DMSO (0.05 mL).

In our previous work on Pd-catalyzed 4-fold dehydrogenative cross-coupling reaction of heterocycles with saturated ketones,[14] we presented detailed mechanistic investigations for the possible reaction pathways of such a catalytic process; finally in situ dehydrogenation of ketones to vinyl ketones[12h,13b,17] followed by olefination of heterocycles was supported. Analogously, to probe the potential intermediates in this transformation, we examined the reaction of mesitylene as well as benzene with freshly prepared nitroethylene under standard conditions. However, neither gave the expected **3a** and **3h**, respectively (eqs 1 and 2, Scheme 3). Yet, we checked the behavior of β-nitroethylbenzene under our standard conditions, which afforded β-nitrostyrene **3h** in 73% yield (eq 3, Scheme 3). These observations demonstrated another possibility that β-nitroethylbenzene, which may be generated via nitro directed β-arylation of nitroethane,[18] might be the intermediate in this transformation. As nitroethylene was reported to be unstable because of its facile polymerization,[19] the in situ dehydrogenation of nitroethane to a nitroethylene intermediate cannot be completely ruled out at present. Detailed studies are needed for insight into the reaction mechanism.

Scheme 3. Mechanistic Experiments



In conclusion, a Pd-catalyzed multidehydrogenative cross-coupling reaction of (hetero)arenes with nitroethane has been developed for the synthesis of β-aryl nitroethylenes that are an important class of synthetic intermediates and biologically active compounds. Importantly, our findings further encouraged us to design and explore such a multidehydrogenation based cross-coupling because it has great potential in enabling the rapid construction of functionalized compounds from simple starting materials in an atom- and step-economical fashion. Further studies to gain a deeper understanding of the reaction mechanism and expand the scope of this transformation are ongoing in our group.

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Supporting Information Available. Detailed experimental procedures and characterization for products. This material is available free of charge via the Internet at http://pubs.acs.org.

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The authors declare no competing financial interest.