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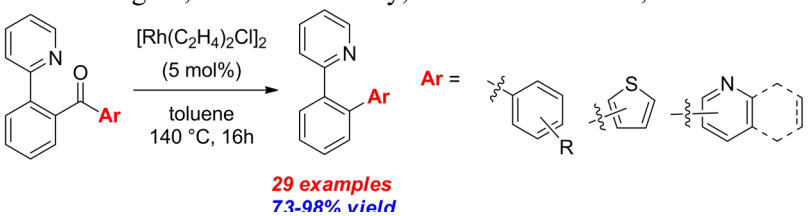

Tetrahedron Letters
journal homepage: www.elsevier.com

Pyridine-directed carbon-carbon single bond activation: rhodium-catalyzed decarbonylation of aryl and heteroaromatic ketones

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ARTICLE INFO

Article history:
Received
Received in revised form
Accepted
Available online

Keywords:
Decarbonylation
Ketone
Carbon-Carbon Bond Activation
Rhodium
Biaryl Coupling

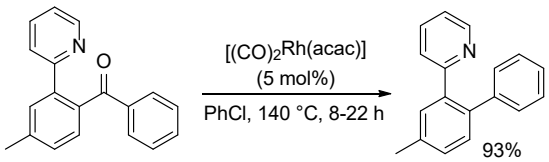
ABSTRACT

The decarbonylation of 2-pyridyl-substituted ketones via transition metal-catalyzed carbon-carbon bond activation provides ready access to a variety of biaryl compounds. The highly efficient and general method provides reliable decarbonylation of benzophenones including a range of functional groups and substitution patterns. The methodology has also proven highly efficient for heteroaromatic substrates, including those containing thiophenyl, indolyl, quinolinyl, and pyridine substitution.

1. Introduction

With the continued development of transition metal catalysis, seemingly impossible transformations have become commonplace. The incredible depth and breadth of methods for the activation of carbon-hydrogen (C-H) bonds has made the process a routine fixture in complex molecule synthesis.[1,2,3,4] The analogous process of carbon-carbon (C-C) bond activation and functionalization promises the means to fundamentally alter the structural framework of organic molecules.[5,6] Although lagging relative to C-H activation, recent efforts have greatly expanded methods for C-C activation,[7] which generally rely on activated substrates[8,9] and/or directing groups[10,11,12,13] to achieve selective reactivity.[14]

One area of significant effort has been the decarbonylation of ketones.[15,16,17] In particular, Sun, Shi, and coworkers reported the extrusion of CO from diaryl and arylalkyl ketones bearing a pyridyl directing group (Scheme 1).[18] Using a $[(CO)_2Rh(acac)]_2$ catalyst, a series of 2-(2-pyridyl)benzophenones were converted into the corresponding biaryl species. In our efforts to expand upon our previously reported carboacylation and ketone exchange chemistry with quinolinyl ketones,[19] we developed complementary pyridyl-directed decarbonylation conditions. Our conditions enable an expansion of the substrate scope relative to that reported by Sun and Shi, including a more benign solvent, a wider scope of regiochemistry, and new functional groups such as amines and thioethers. In addition, we present the decarbonylation of multiple heteroaromatic ketones containing quinoline, indole, furan, and pyridine substitution that highlight the broad utility of the transformation.



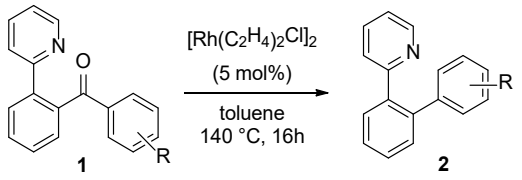
Scheme 1. Sun and Shi's method for rhodium-catalyzed benzophenone decarbonylation.

2. Results and Discussion

Using conditions analogous to those previously utilized by our group for the intramolecular carboacylation of quinolinyl ketones, pyridyl-substituted benzophenones efficiently undergo decarbonylation in the presence of 5 mol% $[Rh(C_2H_2)Cl]_2$ in toluene at 140 °C to produce the corresponding 2-pyridyl-substituted biaryl compounds in high yields. The results in Table 1 demonstrate the generality of the transformation, which includes a variety of electron rich (entries 2-3) and electron deficient (entries 5-6) functional groups. Comparable efficiency is observed substrates containing para, meta, or ortho substitution (entries 3, 7, and 12). Of note, the inclusion of amines (entry 1) and thioethers (entry 4) have not been previously reported in decarbonylation reactions of this nature.

In a similar fashion, decarbonylation proceeds efficiently with compounds containing substitution on the aromatic ring anchoring the pyridine directing group. Again, both electron donating and electron withdrawing substituents readily tolerating the reaction conditions (Table 2). The influence of the directing group is clearly demonstrated in the formation of product **4f**. While the ketone ortho to the 2-pyridyl substituent undergoes efficient decarbonylation, the para acyl group remains unchanged.

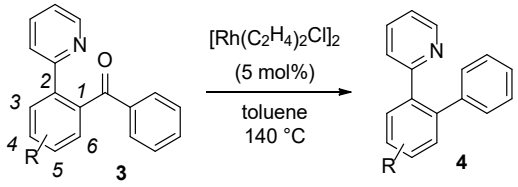
Table 1. Scope of functional group compatibility for decarbonylation reaction.



Entry	Product	R	Yield (%)
1	**2a**	*p*-NMe_2	94
2	**2b**	*p*-OMe	94
3	**2c**	*p*-F	88
4	**2d**	*p*-SMe	86
5	**2e**	*p*-CN	88
6	**2f**	*p*-CF_3	97
7	**2g**	*m*-OMe	98
8	**2h**	*m*-F	91
9	**2i**	*m*-Me	89
10	**2j**	*m*-CF_3	94
11	**2k**	3,5-$(CF_3)_2$	90
12	**2l**	*o*-OMe	88
13	**2m**	*o*-CH_3	79
14	**2n**	*o*-Cl	93

[a] Standard conditions: 0.2 mmol ketone, 0.01 mmol $[Rh(C_2H_4)_2Cl]_2$ in 1.5 mL toluene at 140 °C for 16 hours.

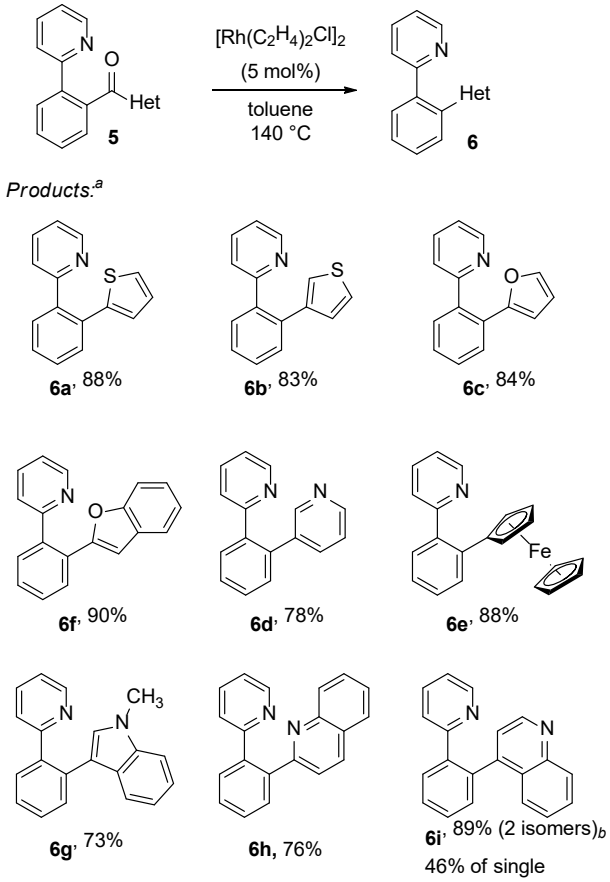
Table 2. Scope of functional group compatibility for decarbonylation reaction.



Entry	Product	R	Yield (%)
1	4a	4-Me	89
2	4b	4-CF_3	92
3	4c	5-OMe	91
4	4d	5-CF_3	94
5	4e	5-CN	83
6	4f	5-$C(O)CH_3$	86

[a] Standard conditions: 0.2 mmol ketone, 0.01 mmol $[Rh(C_2H_4)_2Cl]_2$ in 1.5 mL toluene at 140 °C for 16 hours.

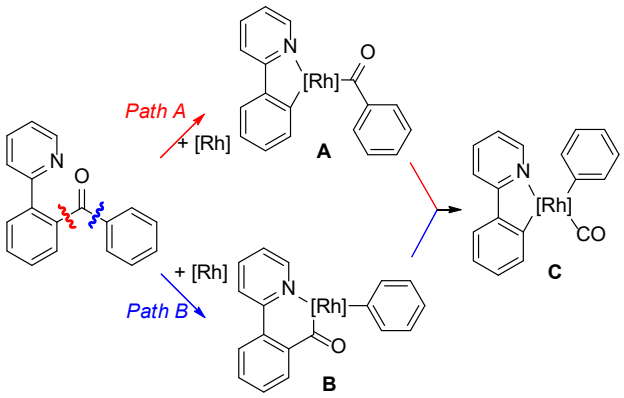
The significant advances presented by this new method are illustrated in Scheme 2, which includes products generated from the successful decarbonylation of heteroaromatic and ferrocenyl species. While previous methods have included furan- and thiophene-containing substrates included here,[16a,18a] this is the first report of the extension of the decarbonylation process to form ferrocenyl compound **5e** and more importantly, to nitrogen-containing heterocycles. While the majority of the ketone substrates are produced through the palladium-catalyzed oxidative coupling of 2-phenylpyridine and a benzaldehyde,[20] this method fails for most nitrogen containing species. Instead, the heterocyclic ketone starting materials are prepared from 2-bromophenyl-2-pyridine via lithium-halogen exchange, nucleophilic addition to an aldehyde, and oxidation.[21] Once formed, decarbonylation of these heterocyclic ketones, including those with pyridine, indole, and quinoline substitution, generally proceeds quite efficiently. Notably, the slightly reduced yields relative to the products in Tables 1 and 2 are attributed to the formation of small amounts of a second isomeric product, quite possibly an atropisomer. In the case of the 4-substituted quinoline **5i**, the isomeric products were a challenge to separate, leading to only 46% of the clean isomer. Efforts are underway to conclusively identify the second isomer and to investigate methods to control the formation of each species.



Scheme 2. Scope of heteroaromatic ketones in the decarbonylation reaction.

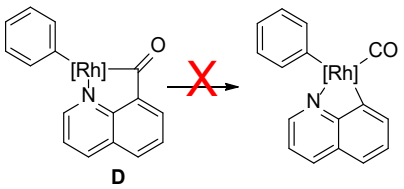
The catalytic process is hypothesized to be similar to that previously proposed by Sun and Shi (Scheme 3).[18] The pyridine directing group is required for reactivity, suggesting that rhodium coordination precedes a sequence of oxidative addition, decarbonylation, and reductive elimination. Notably, the site of initial C-C bond activation is unclear: initial activation may occur on the aryl-ketone bond proximal to the pyridine to generate intermediate **A** (Path A), or it may occur on the bond distal to the pyridine directing group to generate **B** (Path B). Either intermediate is anticipated to undergo decarbonylation to generate rhodium aryl species **C**, which undergoes reductive elimination,

and loss of CO to form the product and regenerate the rhodium catalyst. Further investigation of this mechanism, and particularly the site of C-C activation, is underway.



Scheme 3. Proposed mechanistic pathway.

As described previously, this chemistry stemmed from work on 8-quinolinyl ketones. In direct contrast to the behavior of pyridine-substituted chemistry described here, quinolinyl ketones can undergo addition chemistry following C-C activation without decarbonylation[17,19]. The difference in reactivity is attributed to the chelate that is formed upon oxidative addition. With quinolinyl ketones, rhodium insertion into the C-C bond results in 5-membered Rh(III) metalacycle **D** with an internal carbonyl (Scheme 4). This species does not undergo decarbonylation, as that would form an unfavorable 4-membered chelate. In contrast, the 5-membered-exocyclic carbonyl (Scheme 3, **A**) or the 6-membered-endocyclic carbonyl **B** can each undergo carbonyl migration to generate 5-membered metalacycle **C**. To date, the propensity of the pyridyl-directed ketones to undergo rapid decarbonylation has limited the possibility of any intermolecular chemistry.



Scheme 4. Rationale for lack of decarbonylation with quinolinyl ketones.

In conclusion, our group has developed a highly efficient and general method for ketone decarbonylation that builds upon and broadens the substrate scope of previous methods. These conditions provide reliable decarbonylation of a wide variety of substrates, including numerous heterocyclic ketones, offering new methods for the construction of congested multi-heterocyclic aromatic species.

Acknowledgments

This work was supported by the National Science Foundation (CHE-1148719 and CHE-1764118) and the Henry Dreyfus Teacher-Scholar Award Program (TH-15-030). J.B.J. acknowledges support from the Hope College Schaap Scholars Program. E.A.S acknowledges support from the Arnold and Mabel Beckman Foundation. Grants from the NSF for the purchase of NMR spectrometers (CHE-0922623) and GC/MS instrumentation (CHE-0952768) are also gratefully acknowledged.

Supplementary Material

Supplementary Material for this article, including characterization information of all compounds and complete results of optimization efforts, can be found online.

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