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Rhodium-catalyzed regioselective addition of the *ortho* C–H bond in aromatic amides to the C–C double bond in α,β -unsaturated γ -lactones and dihydrofurans†

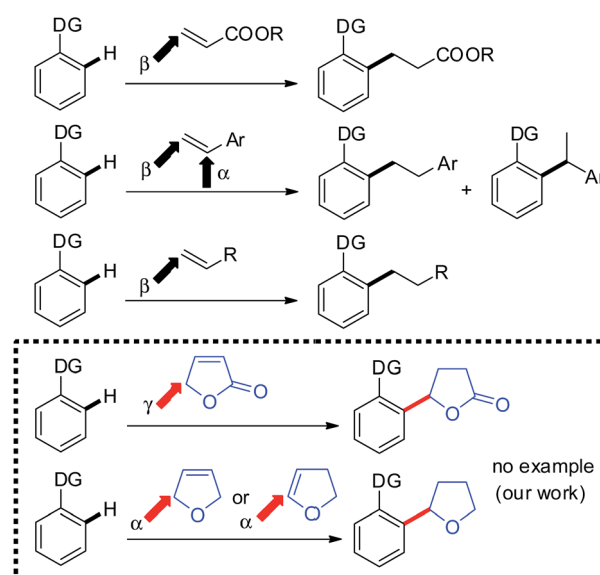
Kaname Shibata and Naoto Chatani*

An unprecedented C–H alkylation using α,β -unsaturated γ -lactones (butenolides) and dihydrofurans was achieved by the Rh-catalyzed reaction of benzamides. C–C bond formation occurs between the *ortho*-position of the benzamide derivative and the γ -position of the butenolide or the α -position of the dihydrofuran. The presence of an 8-aminoquinoline directing group is crucial for the success of the reaction. The results of deuterium labeling experiments indicate that the cleavage of the C–H bond is reversible and suggest that a migratory carbene insertion is involved as the key step.

Introduction

During the past several decades, the chelation-assisted functionalization of C–H bonds has undergone rapid development and is now used in the synthesis of a wide variety of natural products and medicinally relevant compounds.^{1,2} While a wide variety of such functionalizations have been developed to date, the addition of C–H bonds to alkenes represents one of the most fundamental functionalizations of C–H bonds because of its atom economy.^{3,4} While various alkenes can be used as coupling partners, the range of alkenes that are applicable to C–H alkylation remains limited to vinylsilanes and *tert*-butylethylene, which contain no allylic hydrogen, and activated alkenes, such as styrenes and α,β -unsaturated carbonyl compounds. Methodology for using various alkenes as participants in C–H alkylation is still needed. Not only the applicability of alkenes, but also the control of regioselectivity in the addition of C–H bonds to alkenes remains to be solved. Acrylic esters exclusively undergo β -addition reactions to give linear products. In reactions with styrenes, the extent of regioselectivity depends on the catalytic system being used.⁵ In many cases, terminal alkenes containing an allylic hydrogen are not applicable in the reaction, however, Chang and Ackermann recently reported Rh- and Ru-catalyzed alkylation of C–H bonds with various terminal alkenes, in which β -addition takes place with linear products being produced.⁶ We wish to report herein the first example of C–H alkylation of α,β -unsaturated γ -lactones and dihydrofurans, in which C–C bond formation occurs between the *ortho*-

position of an aromatic amide and the γ -position of the butenolide or the α -position of the dihydrofuran, irrespective of the position of the C–C double bond, to give 5-aryl- γ -butyrolactone or 2-aryltetrahydrofuran derivatives, respectively (Scheme 1). These types of products cannot be produced by the alkylation of C–H bonds with alkyl halides. 5-Aryl- γ -butyrolactone derivatives⁷ and 2-aryltetrahydrofuran derivatives⁸ are key structural components of many biologically active and pharmaceutically important molecules, making the construction of such structures synthetically important. Our strategy for constructing 5-aryl- γ -butyrolactone and 2-aryltetrahydrofuran frameworks involves the catalytic activation of a C–H bond in a benzene



Scheme 1 The addition of C–H bonds across alkenes.

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ring, which then adds to the C–C double bond in a butenolide or dihydrofuran derivative. In addition, the directing group can be easily removed or elaborated to another useful functionality.⁹

Results and discussion

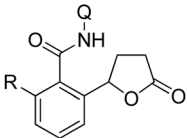
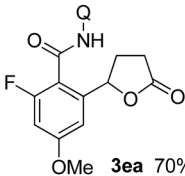
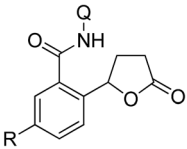
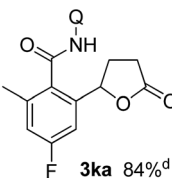
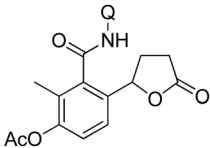
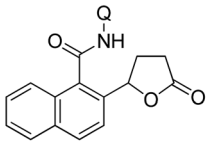
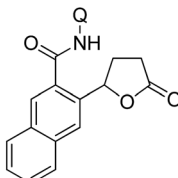
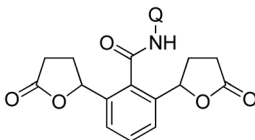
When the butenolide **2a** was used as the coupling partner in the reaction of **1a**, the expected product **4aa** resulting from the reaction at the β -position of the lactone was not obtained, but **3aa** was instead produced as the sole product (Scheme 2). After screening a number of bases, it was found that the reaction is sensitive to the nature of the base used. In general, the use of Na_2CO_3 or K_2HPO_4 gave the best results.¹⁰ To the best of our knowledge, this is the first example of C–H bond alkylation with α,β -unsaturated lactones.

We next examined the effect of the directing group.¹¹ Among the directing groups examined, only 8-aminoquinoline gave the corresponding alkylation product. Most importantly, 2-phenylpyridine, which is an extensively used pyridine directing group in catalytic C–H functionalization reactions, was ineffective. Our research has recently focused on the utilization of an N,N' -bidentate directing chelation system in the functionalization of C–H bonds.^{12,13} This result also shows the potential of such a system for exploring new types of functionalizations of C–H bonds.

Table 1 shows some representative results for the reaction of various aromatic amides with butenolide **2a**. In the case of *meta*-substituted aromatic amides, contrary to the case when methyl acrylate was used in a similar chelation system,^{13a} the alkylation proceeded selectively only at the less hindered position, as in **3fa**–**3ja**, because the introduced lactone moiety is a sterically demanding group compared with the acrylate moiety. In the case of the benzamide **1o**, both *ortho* C–H bonds underwent alkylation to give the double alkylation product **3oa** in 61% isolated yield.

Substituted α,β -unsaturated γ -lactones **2** were also applicable to the present reaction (Table 2). Me, Bu, and benzyl substituted lactones could all be used, as in **3ab**, **3ac**, and **3ad**. In all cases, a mixture of *cis* and *trans* isomers was produced in a comparable ratio. The ratio was constant even when the reaction was stopped after a short reaction time, suggesting that the ratio obtained is a thermodynamic ratio. Lactones bearing

Table 1 Rh-catalyzed alkylation of aromatic amides **1a**–**1o** with butenolide **2a**^{a,b}

| | | | | |
|--|---|--|---|-----------------------------|
|  | R = Me R = Ph R = CF ₃ R = F | 3aa 82% ^{c, d} 3ba 73% 3ca 74% 3da 58% |  | 3ea 70% ^c |
|  | R = Me R = OMe R = Ph R = CF ₃ R = C(O)CH ₃ | 3fa 72% ^{c, d} 3ga 34% 3ha 87% ^d 3ia 69% 3ja 49% ^d |  | 3ka 84% ^d |
|  | | 3la 67% ^d |  | 3ma 63% ^d |
| | | |  | 3na 65% ^d |
|  | | 3oa 61% | | |

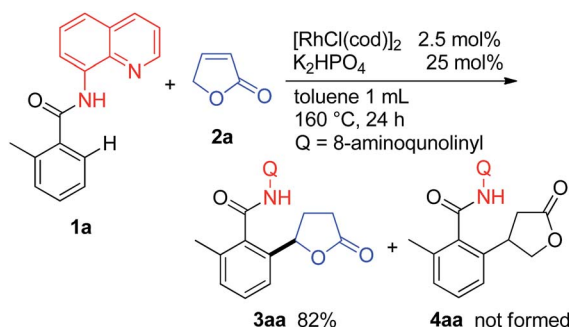
^a Reaction conditions: amide **1** (0.3 mmol), lactone **2a** (0.9 mmol), $[\text{RhCl}(\text{cod})]_2$ (0.015 mmol), Na_2CO_3 (0.075 mmol), toluene (1 mL), at 160 °C for 24 h. ^b Isolated yields. ^c Lactone (0.6 mmol) and $[\text{RhCl}(\text{cod})]_2$ (0.0075 mmol) were used. ^d K_2HPO_4 was used in place of Na_2CO_3 .

functional groups on the phenyl ring, such as Br and MeO, were tolerated under the reaction conditions.

The 2,3-dihydrofuran **5a** and the 2,5-dihydrofuran **5b** also participated in the alkylation reaction (Table 3). When the reaction was carried out under two different sets of conditions, *i.e.* methods A and B, marginal effects were observed. Irrespective of the position of the olefin as in **5a** and **5b**, C–C bond formation took place at the α -position (next to the oxygen atom) of the dihydrofuran.¹⁴

The results for the reaction of *meta*-substituted benzamides with **5a** are shown in Table 4. The reaction was carried out under the reaction conditions of method B. Irrespective of the electronic nature of the substituent, only the less hindered C–H bonds reacted.

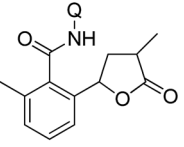
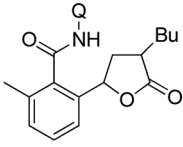
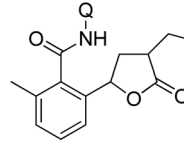
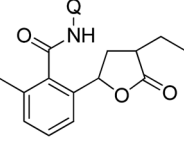
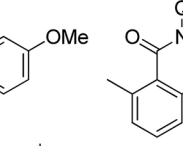
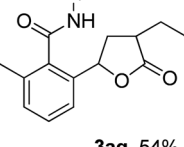
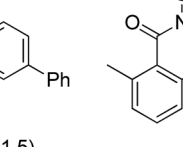
To gain insights into the reaction mechanism, deuterium labeling experiments were carried out in the absence of alkene (Scheme 3a). Irrespective of the reaction conditions (method A: KOAc and method B: PivOH), a significant amount of H/D exchange occurred even within a short reaction time (15 min), and the exchange occurred only at the *ortho* position (Scheme 3a), indicating that the cleavage of the C–H bond is reversible and does not appear to be the rate-determining step. The reaction of **1a** in toluene-*d*₈ was carried out. No deuterium atom was incorporated into the product, indicating that in the H/D



Scheme 2 Rh-catalyzed C–H alkylation of **1a** with butenolide **2a**.



Table 2 Rh-catalyzed alkylation of aromatic amide **1a** with α,β -unsaturated γ -butyrolactones **2b–2h**^{a,b}


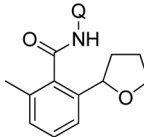

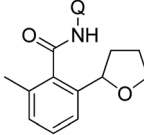

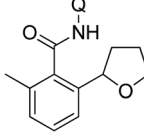

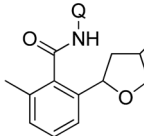
| | | |
|---|---|---|
|  |  |  |
| 3ab 59% (1:1.7) | 3ac 60% (1:1.5) | 3ad 80% (1:1.5) ^c |
|  |  | |
| 3ae 67% (1:1.6) ^d | 3af 54% (1:1.5) | |
|  |  | |
| 3ag 54% (1:1.5) | 3ah 67% (1:1.4) | |

^a Reaction conditions: amide **1** (0.3 mmol), lactone **2a** (0.9 mmol), [RhCl(cod)]₂ (0.015 mmol), K₂HPO₄ (0.075 mmol), toluene (1 mL), at 160 °C for 24 h. ^b Isolated yields. The number in parentheses denotes the ratio of *cis* and *trans* isomers. ^c The reaction was run for 12 h. ^d KOAc was used in place of K₂HPO₄.

exchange reaction, the proton source is not the solvent, but rather, that the proton comes from the NH bond in the substrate (scheme not shown). When the reaction was carried out in the presence of dihydrofuran **5a** (Scheme 3b), alkylation product **6aa–d** was obtained in 7% and 32% NMR yield, depending on the additive used, along with recovery of the starting material **1a–d**. Curiously and unexpectedly, a deuterium atom was incorporated into the THF ring only at the α -position and no deuterium atoms were detected at any of the other positions in the THF ring by ¹H NMR. Both the *ortho*-carbon and hydrogen atom in the benzamide attach to the α -carbon of the THF ring. A similar result was obtained even when 2,5-dihydrofuran (**5b**) was used as the coupling partner (Scheme 3c). To exclude the possibility that H/D exchange occurs at the α -position of the THF ring under the reaction conditions employed, **6aa** was reacted with CD₃COOD at 160 °C in the presence of a rhodium complex. However, no deuterium was introduced into **6aa** (scheme not shown). These results suggest that the *ortho* C–H bond appears to undergo a migratory carbene insertion, as discussed later.

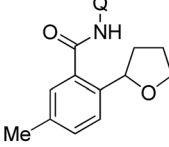
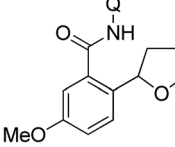
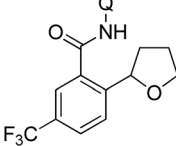
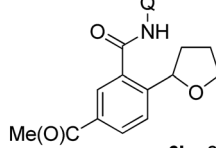
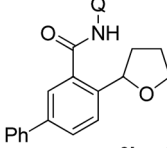
Based on our previously reported studies^{13a,b} and the results obtained in the present work, a proposed mechanism for the reaction is shown in Scheme 4. The coordination of the quinoline nitrogen in the aromatic amide **1** to give a Rh(I)X species, followed by the oxidative addition of an N–H bond, gives complex **A**.¹⁵ The insertion of **5a** into the H–Rh bond in **A** gives complex **B**, which, after the elimination of HX, affords the carbene complex **C**.¹⁶ The migratory insertion of the *ortho* C–H bond to a carbene moiety in the complex **C** through the

Table 3 Rh-catalyzed alkylation of aromatic amide **1a** with dihydrofurans **5a–5d**^{a,b,c}

| alkene | product | |
|---|---|--|
|  |  | 6aa 69% ^a 6aa 80% ^b |
|  |  | 6aa 74% ^a 6aa 68% ^b |
|  |  | 6ac 76% (1:1.3) ^a 6ac 70% (1:1.5) ^{b,d} |
|  |  | 6ad 79% (1:1.1) ^a 6ad 76% (1:1.3) ^b |

^a Reaction conditions (method A): amide **1a** (0.3 mmol), dihydrofuran (0.6 mmol), [RhCl(cod)]₂ (0.0075 mmol), KOAc (0.075 mmol), toluene (1 mL), at 160 °C for 12 h. ^b Reaction conditions (method B): amide **1a** (0.3 mmol), dihydrofuran (0.6 mmol), [Rh(OAc)(cod)]₂ (0.0075 mmol), PivOH (0.3 mmol), toluene (1 mL), at 160 °C for 12 h. ^c Isolated yields. The number in parentheses denotes the ratio of *cis* and *trans* isomers. ^d NMR yield.

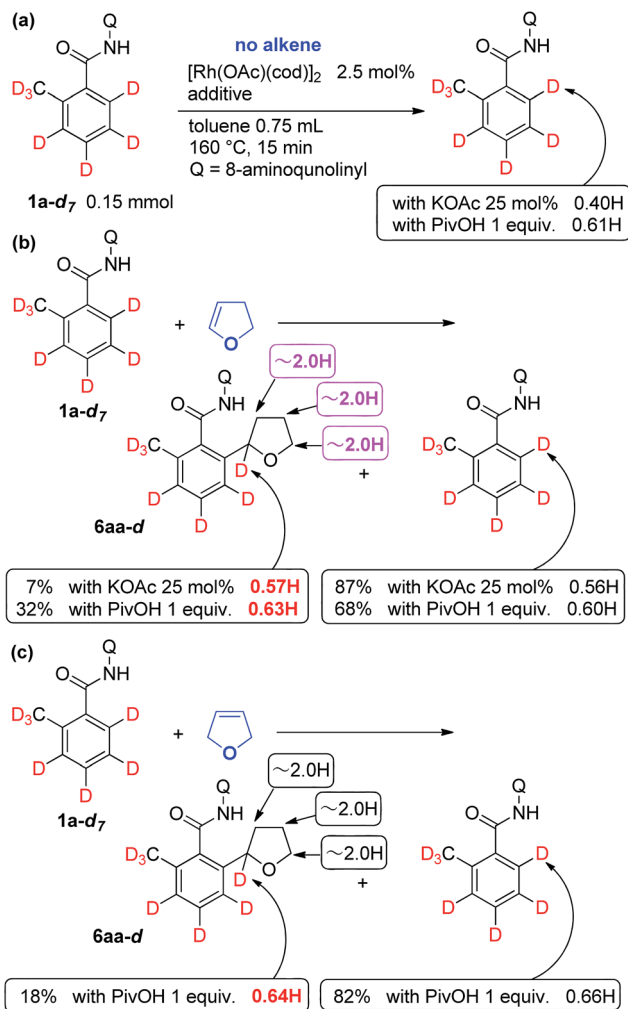
Table 4 Rh-catalyzed alkylation of *meta*-substituted aromatic amides with 2,3-dihydrofuran **5a**^{a,b}

| | | |
|--|---|---|
|  |  |  |
| 6fa 89% | 6ga 59% | 6ia 77% |
|  |  | |
| 6ja 83% ^c | 6ha 80% | |

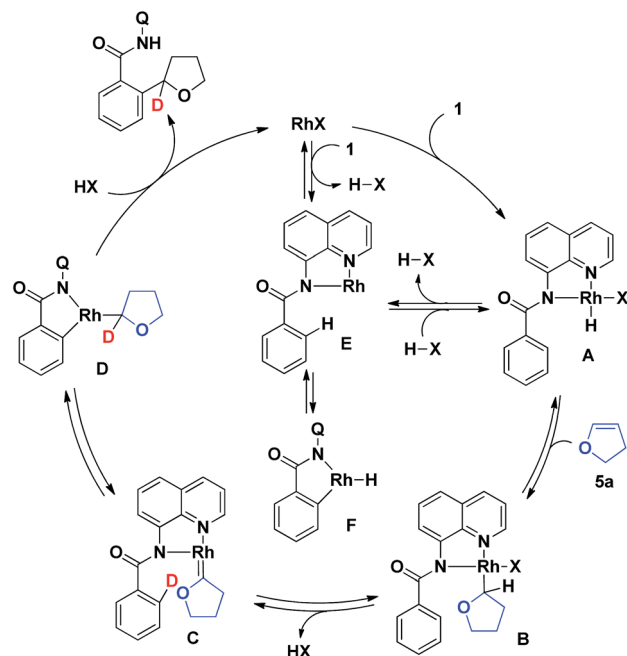
^a Reaction conditions: amide **1** (0.3 mmol), dihydrofuran (0.6 mmol), [Rh(OAc)(cod)]₂ (0.0075 mmol), PivOH (0.3 mmol), toluene (1 mL), at 160 °C for 12 h. ^b Isolated yields. ^c [Rh(OAc)(cod)]₂ (0.015 mmol) for 24 h.

oxidative addition of the *ortho* C–H bond followed by α -hydride migration gives **D**,^{17,18} which undergoes reductive elimination followed by protonation to give the final product with regeneration of the Rh(I) species. An alternative mechanism for

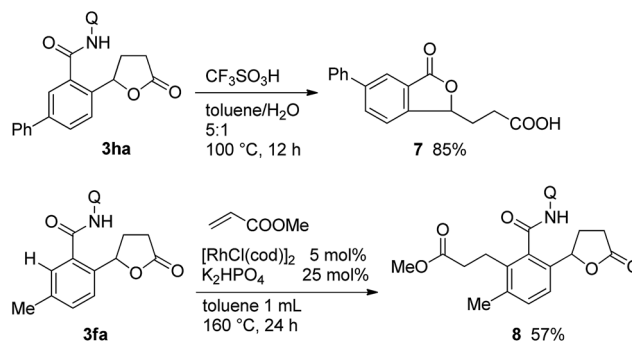




Scheme 3 Deuterium labeling experiments.



Scheme 4 Proposed mechanism.



Scheme 5 Synthetic applications.

generating the complex **A** involves the coordination of a quinoline nitrogen to the Rh(i) center, a ligand exchange to generate the Rh(i) complex **E** with the concomitant generation of HX, followed by the reaction of the complex **E** with HX. The *ortho* C–H bond of complex **E** then undergoes a reversible oxidative addition to the rhodium center to form the cyclometalated Rh–H complex **F**, the formation of which accounts for the reversibility of the cleavage of the C–H bond at the *ortho* position of the benzamide.¹⁹ As shown in Scheme 3b, deuterium was only incorporated at the α -position of the THF ring of the product. The proposed mechanism involving the formation of the intermediate carbene complex **C** is consistent with the deuterium labeling data shown in Scheme 3b, although no direct experimental evidence for this exists. To better understand the details of the reaction mechanism, more experiments including DFT calculations will be needed.

Scheme 5 shows the potential synthetic utility of the C–H bond alkylation reaction. The treatment of **3ha** under acidic conditions gave the isobenzofuran-1(3*H*)-one derivative **7** in 85% isolated yield. The present protocol was also applicable to the preparation of highly substituted and/or functionalized

5-aryl- γ -butyrolactone derivatives. When the lactone **1f** was used in the reaction, the mono-alkylated product **3fa** was exclusively formed, as shown in Table 1. The remaining hindered *ortho*-C–H bond in **3fa** could be successfully alkylated with methyl acrylate in the presence of a rhodium catalyst^{13a} to give compound **8**, which contains three different adjacent carbonyl functional groups on the benzene ring.

Conclusion

In summary, this reaction represents the first example of C–H alkylation with butenolides, in which C–C bond formation occurs between the *ortho*-position of an aromatic amide and the γ -position of a butenolide derivative. In addition, dihydrofurans can also be used in the alkylation reaction, in which case, C–C bond formation occurs between the *ortho*-position of the aromatic amide and the α -position of the dihydrofuran, irrespective of the position of the C–C double bond. The use of an



8-aminoquinoline moiety as a directing group is crucial for the success of the reaction. In fact, the reaction with 2-phenylpyridine, which has been used extensively as a substrate for a wide variety of functionalizations of C–H bonds, did not succeed. The functionalization of C–H bonds using an *N,N'*-bidentate directing group began to appear in the literature only in the last ten years, since Daugulis reported the Pd(II)-catalyzed arylation of C–H bonds in aliphatic amides in 2005.²⁰ Since then, it has been shown that various transition metal complexes can be used in the *N,N'*-bidentate chelation system.¹² As more mechanistic information emerges, new and more exciting advances can be anticipated.²¹

Acknowledgements

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