

Chemistry of 1,2-allenyl/propargyl metal species. A personal account*

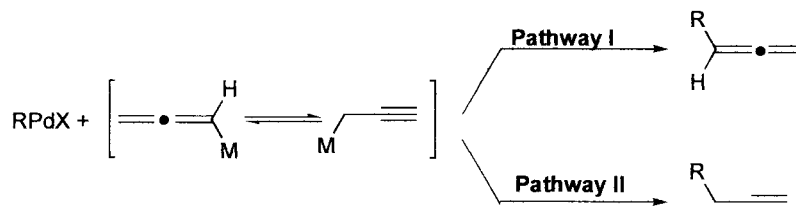
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Abstract: The Pd(0)-catalyzed coupling reaction of aryl and electron-deficient alkenyl halides with the organozinc reagents formed by the subsequent treatment of 1-phenylalk-1-ynes with *n*-BuLi and ZnBr₂ with or without a catalytic amount of HgCl₂ was studied. Both the allene-formation- and the alkyne-formation-type coupling reactions were observed, depending on the structures of organic halides and 1-arylalk-1-ynes.

INTRODUCTION

Cross-coupling reaction between an organometallic reagent and R'X (R' = alkenyl, aromatic) with a transition-metal catalyst is one of the best ways for the formation of C-C bonds because of the easy availability of both reactants [1]. For the coupling reaction between an organic halide and an allenic/propargylic metallic reagent, there are, in principle, two possibilities: (1) the formation of allenes (Pathway I); (2) the formation of alkynes (Pathway II) (Scheme 1).



Scheme 1

Recently, we have developed a HgCl₂-catalyzed monolithiation reaction of 1-arylalk-1-ynes. Polyolithiation was avoided by using a catalytic amount of HgCl₂ [2]. The subsequent reaction of the lithium reagent formed in situ with benzylic [3] and allylic halides [4] afforded substituted 1-aryl-1-alkynes or 1-phenyl-1,2-allenes in good yields. In this account, we will summarize our recent results on the Pd(0)-catalyzed coupling reaction of aryl and alkenyl halides with allenic/propargylic zinc reagents formed via the transmetalation reaction on the basis of the above monolithiation reaction.

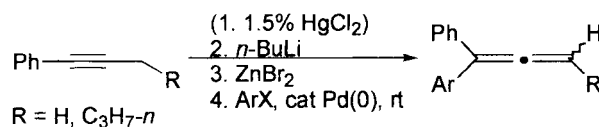
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RESULTS AND DISCUSSION

Pd(0)-catalyzed coupling reaction of aryl halides with allenic/propargylic zinc reagents [5]

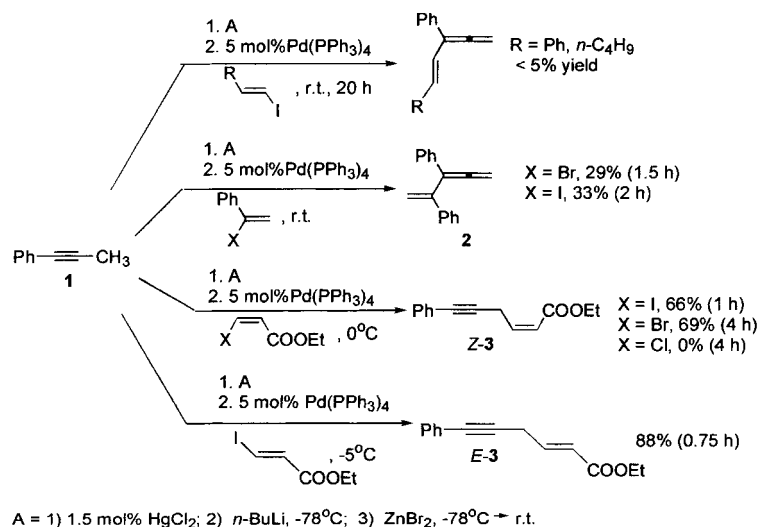
With the addition of 1.5 molar equiv of ZnBr_2 after the lithiation of 1-phenylalk-1-yne in the presence of 1.5 mol % HgCl_2 , the organozinc reagents thus formed by transmetalation reacted smoothly with aryl halides under the catalysis of $\text{Pd}(\text{PPh}_3)_4$ to afford 1,2-diaryl-1,2-dienes in moderate to good yields with excellent selectivity, i.e., the pathway II-type alkynic products were not formed. For this reaction, it is also interesting to observe that the reaction can proceed in the absence of HgCl_2 , indicating ZnBr_2 played a similar role in monolithiation as HgCl_2 did, but HgCl_2 had a more dramatic effect on the monolithiation of 1-phenyl-1-alkynes (Scheme 2). Moreover, in most cases the reactivity of $\text{Pd}(\text{PPh}_3)_4$ is higher than that of $\text{PdCl}_2(\text{PPh}_3)_2$.



Scheme 2

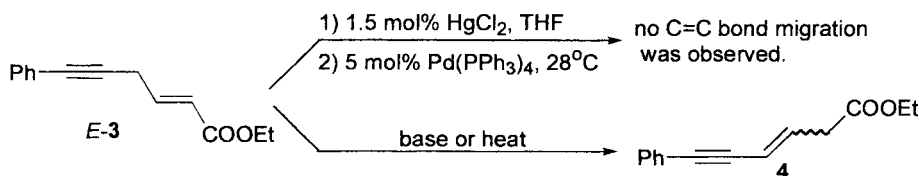
Pd(0)-catalyzed coupling reaction of electron-deficient alkenyl halides with allenic/propargylic zinc reagents [6]

Under the same conditions, (*E*)-1-iodohexene and (*E*)-1-iodostyrene did not afford the corresponding cross-coupling product in decent yields. When α -bromostyrene or α -iodostyrene was used, it afforded 2,3-diphenyl-1,3,4-pentatriene in 29% and 33% yields, respectively. Here it is important to note that the coupling reaction afforded the Pathway I-type allenic product, which is inconsistent with the results of aryl halides. But to our surprise, the corresponding reaction of ethyl (*Z*)-3-iodopropenoate afforded a Pathway II-type product, i.e., ethyl 6-phenylhex-5-yn-2(*Z*)-enoate, exclusively. The configuration of $\text{C}=\text{C}$ bond remained intact (Scheme 3). (*Z*)-3-Iodopropenenitrile reacted similarly with the organozinc reagent formed by the subsequent reaction of 1-phenyl-1-propyne, *n*-BuLi, and ZnBr_2 in the presence of HgCl_2 under the catalysis of $\text{Pd}(\text{PPh}_3)_4$ to afford 6-phenylhex-5-yn-2(*Z*)-enitrile.



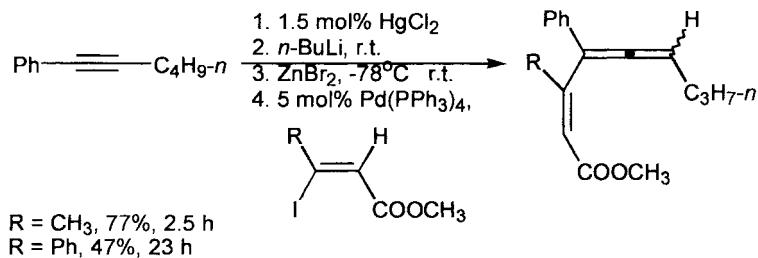
Scheme 3

In most cases, the results with HgCl_2 are somewhat better. The excess amount of the zinc reagent and the temperature of the coupling reaction were found to be responsible for the migration of the C=C double bond in this reaction (Scheme 4).



Scheme 4

On the other hand, it is interesting to observe that by starting from 1-phenylhex-1-yne, the corresponding reaction afforded allenic products, exclusively. Moreover, both ethyl (*Z*)-3-iodopropenoate and ethyl (*E*)-3-iodopropenoate produced the same product, i.e., ethyl 4-phenyl-2(*E*),4,5-nonatrienoate in 73% and 86% yields, respectively. With $\text{R} = \text{CH}_3$ or Ph , the configuration of C=C bond remained (Scheme 5).



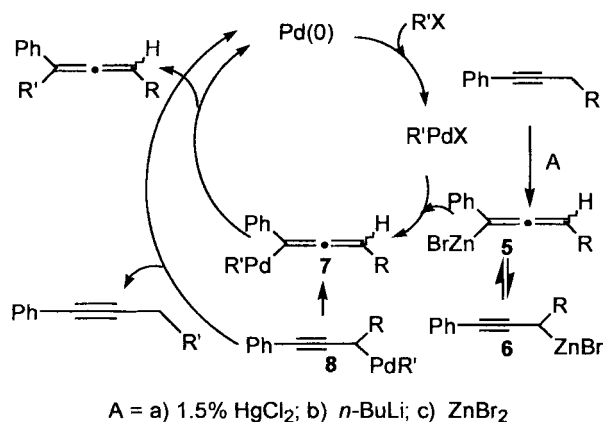
Scheme 5

Mechanism of coupling reaction

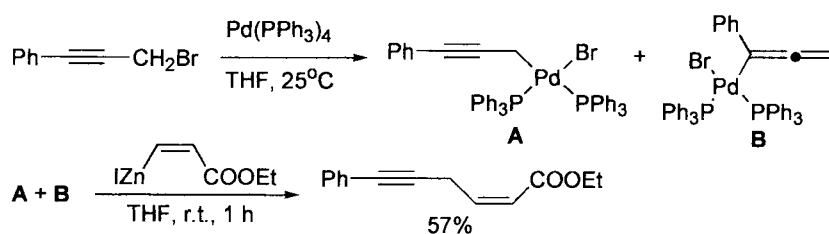
From the above results, it is obvious that the structure of organic halides and 1-arylalk-1-yne affected the regioselectivity of this reaction greatly. A plausible mechanism is the oxidative addition reaction of an organic halide with $\text{Pd}(0)$ to form an organopalladium intermediate RPdX , which would be trapped by the allenic/propargylic zinc reagents formed by the transmetalation reaction of the organolithiums with ZnBr_2 to afford the allenic palladium and the propargylic palladium species, respectively. For the aryl halide, rearrangement of the propargylic aryl palladium intermediate **8** to the allenic aryl palladium intermediate **7** [7] followed by a reductive elimination reaction produced 1,1-diaryl-1,2-diene as the sole product and regenerated the zero-valent Pd catalyst (Scheme 6).

In the literature it has been reported that in most cases the oxidative addition reaction of $\text{Pd}(0)$ with allenic bromides or propargylic halides afforded completely or predominantly η^1 -allenyl palladium species. However, the equilibrium between η^1 -allenyl palladium, η^1 -propargyl palladium, and η^3 -propargyl palladium complexes depends on the ligands used as well as the substituents at the propargyl moiety. For the allenic halide, with 3-phenylprop-1-yne, 6-phenylhex-5-yn-2-enoates were formed via the reductive elimination of η^1 -propargyl-type of palladium intermediate **8** [7], while with 1-phenylhex-1-yne, probably due to the steric hindrance of R , 2,4,5-trienoates were formed exclusively via the reductive elimination of η^1 -allenyl-type of palladium intermediate **7** (Scheme 6).

From the above plausible mechanism, the different regioselectivity may be derived from the competing reactivity of either two isomeric organozincs or two isomeric palladium species. Indeed, the reaction of a mixture of η^1 -propargylic palladium complex **A** and η^1 -allenyl palladium complex **B** (ratio: $\text{A/B} = 1.7/1$) [8] with ethoxycarbonyl ethenyl zinc iodide afforded alkynic product ethyl 6-phenylhex-5-yn-2(*Z*)-enoate, exclusively [9] (Scheme 7).



Scheme 6



Scheme 7

In conclusion, we have observed two different types of coupling patterns for the Pd(0)-catalyzed reaction of allenic/propargylic zinc reagents with organic halides. The regioselectivity of the coupling reaction depends not only on the structure of organic halides, but also on that of 1-aryllalk-1-yne. The further study is being investigated in our group.

ACKNOWLEDGMENTS

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7. It should be noted that under Procedure A, 1-phenylprop-1-yne afforded a mixture of allenic and propargylic zinc reagents; see ref. 5.
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