

パラジウム錯体触媒を用いたアリルエステルと末端アルキンの
一酸化炭素挿入を伴うカップリング反応

Carbonylative Coupling of Allyl Esters with Terminal Alkynes Catalyzed by Palladium Complexes

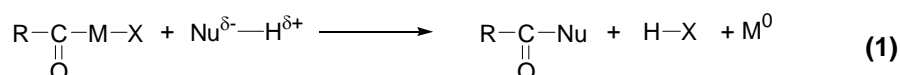
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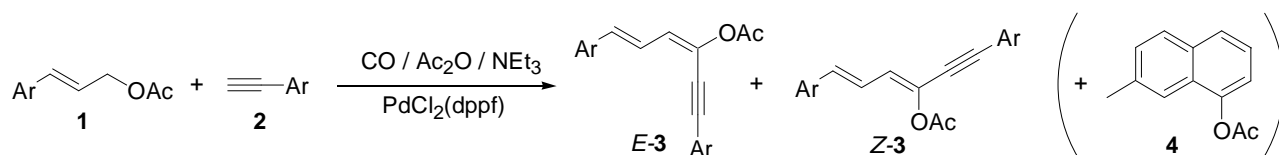
Abstracts; Carbonylative coupling of cinnamyl acetates with aryl alkynes in the presence of catalytic amount of palladium-dppf (1,1'-bis(2,2,6,6-tetramethylpiperidine-3-yl)ethane) complex gave 1,6-diaryl-4-acetoxy-1,3-hexadien-5-yne in moderate yield. *Sample*

Introduction

Transition metal catalyzed carbonylation reactions in homogeneous phase have been widely investigated and utilized in synthetic organic chemistry. One of their key steps involves the reaction between acyl-metal intermediate and nucleophiles to release the product¹⁾ (Eq. 1).



In the course of our study on Pd-catalyzed carbonylation reactions, we found that cinnamyl acetates (**1**) and arylalkynes (**2**) can be successfully converted to 1,6-diaryl-4-acetoxy-1,3-hexadien-5-yne (*E*-**3** and *Z*-**3**) accompanying CO insertion (Scheme 1.). Herein we report our preliminary results.



Scheme 1. Ar = *p*-tolyl

Results

Results were summarized in Table 1. When reactions were carried out at 80 or 100°C, *E*-**3** and *Z*-**3** were obtained in 30-60% yield with a small amount of **4** (Run 1-6). X-ray crystallographic analysis showed that they are the *E*- and *Z*- isomers around the double bond between C(3) and C(4) of hexadienyne framework (Figure 1.). The *E/Z* ratios were around 1:1 and this value was not so much affected by the reaction time or the temperature. When the reaction was performed at higher temperature i.e. 120°C, total yield of *E*-**3** and *Z*-**3** decreased to 15-32% with smaller content of *E*-**3** (Run 7-9). On the other hand, the formation of **4** became pronounced at this temperature. On the other hand, the formation of **4** became pronounced at this temperature.

Table 1. Carbonylative coupling of **1** with **2**.^a

Run	Temp.	Time /h	Yield ^b /%	Products ratio ^c		
	/°C			<i>E-3</i>	<i>Z-3</i>	4
1	80	5	52	0.92	1.00	0.03
2		10	59	0.95	1.00	0.04
3		20	61	0.99	1.00	0.06

^aReaction conditions; **1** 1.0mmol, **2** 1.1mmol, PdCl₂(dppf) 0.01mmol, Ac₂O 2.1mmol, NEt₃ 2.1mmol,

Discussion: Reaction mechanism

A plausible pathway for the present reaction is shown in **Scheme 4**. Pd-dppf catalyst is reduced to Pd(0) under the reductive reaction conditions. Cinnamyl acetates oxidatively add to the Pd(0) to give either σ - or π -allyl Pd intermediate. CO insertion into the Pd-C bond results in the formation of *E*-butenoyl-Pd intermediate.....

Scheme 4. Ar = *p*-tolyl. Ligands around Pd were omitted.

Conclusion

We have revealed that it is possible to synthesize 1,6-diaryl-4-acetoxy-1,3-hexadien-5-ynes by Pd-catalyzed carbonylative coupling of cinnamyl acetates with arylalkynes. From our preliminary results, this reaction is applicable to

References

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