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Preliminary communication

PALLADIUM-CATALYZED ACYL—O BOND FISSION—PHENYLATION REACTION OF ALLYL ESTERS WITH BENZENE

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Summary

The palladium-catalyzed acyl—O bond fission—phenylation reaction of allyl esters with benzene has been found to give cinnamaldehyde derivatives in one step in modest yields.

In 1967 we reported a new substitution reaction of aromatic compounds for hydrogen on the double bond of olefins [1]. This is a general reaction occurring between olefins, acyclic and cyclic, and aromatics, both benzenoid and nonbenzenoid, and provides a very convenient synthetic organic method [2].

In connection with this reaction we have examined Pd-mediated acyl—O bond cleavage of allyl esters in the hope of exploring a new reaction in which both arylation and acyl—O bond cleavage take place. We found that the $Pd(CF_3CO_2)_2/CF_3COOH$ system gives rise to cinnamaldehyde derivatives from allyl esters and benzene.

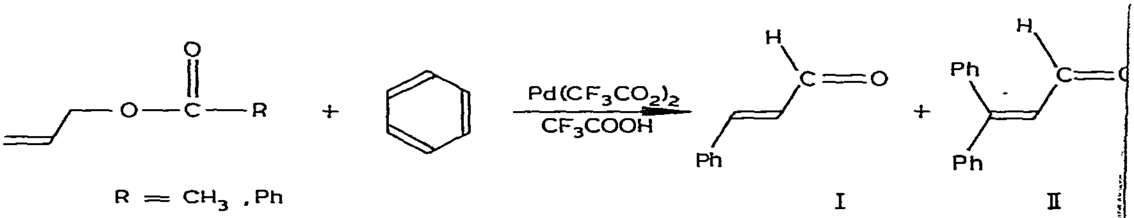

Table 1 lists the results of Pd-mediated acyl—O bond fission—phenylation reactions of allyl acetate and benzoate with benzene. The data in this Table deserve some comments. The $Pd(CF_3CO_2)_2/CF_3COOH$ system is the most

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TABLE 1

REACTIONS OF ALLYL ESTERS WITH BENZENE IN THE PRESENCE OF PALLADIUM(II) CARBOXYLATES AND CF_3COOH [a]

Run	Pd^{II} salt	Allyl ester	Product yield (%) [b]	
			I	II
1	$Pd(CF_3CO_2)_2$	allyl acetate	trace	47 [c]
2	$Pd(CH_3CO_2)_2$	allyl acetate	4	17 [c]
3	$Pd(CH_3CO_2)_2$ [d]	allyl acetate	trace	34
4	$Pd(CF_3CO_2)_2$	allyl benzoate	4	35
5	$Pd(CH_3CO_2)_2$	allyl benzoate	12	9 [e]
6	$Pd(CH_3CO_2)_2$ [d]	allyl benzoate	2	39 [f]

[a] Reactions were performed charging 0.5 mmol of palladium carboxylate, 0.5 mmol of allyl ester in 5 ml of benzene and 1.25 ml of trifluoroacetic acid with stirring at 80°C for 8 h. [b] Yields are based upon the starting allyl ester and determined by VPC. [c] Biphenyl was also formed in 2% yield. [d] 4 mol equiv to palladium salt of sodium acetate was employed. [e] A 9% yield of biphenyl was also formed. [f] A 1% yield of biphenyl was also formed.

TABLE 2

CATALYTIC ACYL—O BOND FISSION—PHENYLATION REACTION OF ALLYL ACETATE WITH BENZENE [a]

Pd^{II} salt (mmol)		Reaction time (h)	Product yield (%) [b]	
			I	II
$Pd(CH_3CO_2)_2$	0.050	8	133	107
$Pd(CH_3CO_2)_2$	0.050	24	116	18
$Pd(CH_3CO_2)_2$	0.025	7	275	—
$Pd(CH_3CO_2)_2$	0.010	7	366	—
$Pd(CF_3CO_2)_2$	0.050	24	121	9

[a] Reactions were performed charging 0.5 mmol of allyl acetate, 2.0 mmol of p-benzoquinone as a reoxidizing agent in 5 ml of benzene and 1.25 ml of trifluoroacetic acid with stirring at 80°C. [b] Yields are based upon the palladium catalyst and determined by VPC using an internal standard.

effective for the acyl—O bond fission—phenylation of allyl acetate and benzoate (runs 1 and 4). However, the $Pd(CH_3CO_2)_2/CF_3COOH$ system is also active for the reaction (runs 2 and 5) whereas the $Pd(CH_3CO_2)_2/CH_3COOH$ system does not cause the reaction*. Addition of sodium acetate to the $Pd(CH_3CO_2)_2/CF_3COOH$ system increases the yields of aldehydes (runs 3 and 6). This reaction can be made catalytic with respect to palladium when *p*-benzoquinone is employed as a reoxidizing agent**. Table 2 shows some examples. By using this reaction one can prepare cinnamaldehyde derivatives from allyl esters and benzene in one step. Control experiments revealed that β-phenyl cinnamaldehyde (II) was formed from the further phenylation of

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*The reactions of allyl acetate and benzoate with benzene in the $Pd(CH_3CO_2)_2/CH_3COOH$ system give cinnamyl acetate (64%) and cinnamyl benzoate (65%) as main products, respectively, and no aldehyde derivatives were obtained at all: Y. Fujiwara, M. Yoshidomi, unpublished results.

**Palladium(II) is needed for the phenylation of olefins [2] although palladium(0) may be responsible for the acyl—O bond cleavage.

the initially formed cinnamaldehyde (I). The mechanism of this novel reaction, especially that of the acyl—O bond cleavage, is not yet clear at this stage. However, the fact that at least CF_3COOH or $Pd(CF_3CO_2)_2$ is needed to cause the reaction suggests that an acetate or benzoate group in allyl esters is replaced with a trifluoroacetate group [3]. In fact allyl trifluoroacetate and cinnamyl trifluoroacetate reacted with benzene with acyl—O bond cleavage even in the $Pd(CH_3CO_2)_2/CH_3COOH$ system to give I and II. Two mechanisms may be considered. One involves oxidative addition of an acyl—O bond of the esters to palladium(0) to form an intermediate $CH_2{=}CHCH_2{-}O{-}Pd{-}C(O){-}CF_3$* and the other involves hydrolysis of the esters to allyl alcohol and its subsequent oxidation and phenylation. We favor the former on the basis that when allyl alcohol was allowed to react with benzene under the similar reaction conditions, only a 3% yield of I was obtained without the formation of II.

Typically, $Pd(CF_3CO_2)_2$ (0.5 mmol), allyl acetate (0.5 mmol), benzene (5 ml), and CF_3COOH (1.25 ml) were placed in a 50ml-centrifuge tube containing a magnetic stirring bar. After the tube was sealed with a No-Air stopper, the mixture was heated at reflux with stirring for 8 h. After work-up the products were analyzed and separated by VPC to give II (47%) and a trace amount of I (Table 1 run 1).

Although it is known that allyl esters such as allyl acetate undergo allyl—O bond cleavage with transition metals like palladium to give π-allylpalladium complexes which further react with various nucleophiles [2c,4], acyl—O bond cleavage by palladium has never been observed.

We are currently extending our studies to other esters in order to develop a new synthetic procedure for arylated olefinic aldehydes via the acyl—O bond fission—arylation reactions.

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*Oxidative addition of aryl carboxylates at the acyl—O bond is reported in the reactions of aryl carboxylates with bis(1,5-cyclooctadiene)nickel complexes: T. Yamamoto, J. Ishizu, T. Kohara, S. Komiya, and A. Yamamoto, J. Amer. Chem. Soc. 102 (1980) 3758.