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PALLADIUM-PROMOTED REACTION OF ALLYL TRIMETHYLSILYL ETHERS WITH ARYL IODIDES

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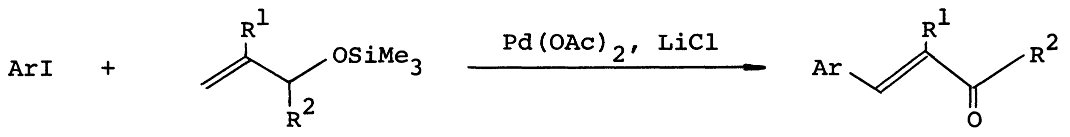
Allyl trimethylsilyl ether reacts with aryl iodides in the presence of palladium acetate and lithium chloride to afford selectively β-aryl (E)-α,β-unsaturated carbonyl compound.

It has been reported that the γ-arylation of allylic alcohols with aryl halides is catalyzed by palladium catalysts to produce β-arylaldehydes and ketones.[1] It would be useful to convert allylic alcohols into α,β-unsaturated carbonyl compounds. Herein, we wish to report the synthesis of β-aryl α,β-unsaturated carbonyl compounds by the palladium-promoted arylation of allyl trimethylsilyl ethers.

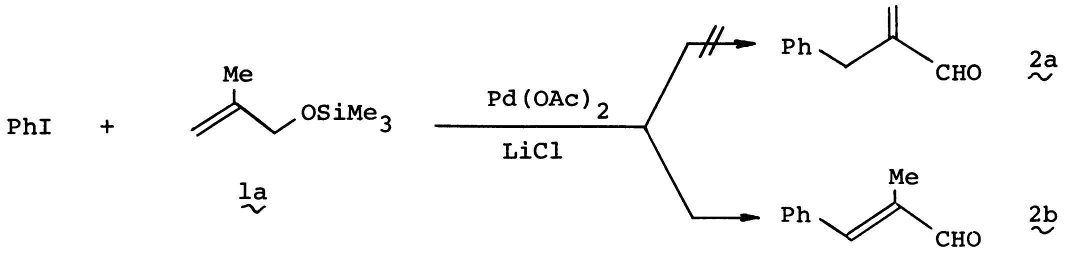


1

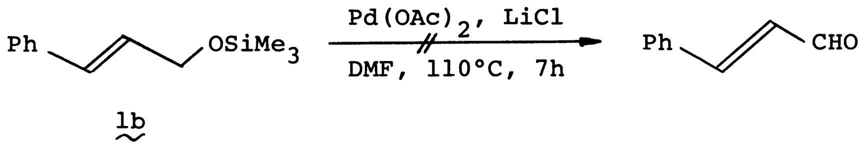
2

The general experimental procedure is as follows. To a stirring solution of $Pd(OAc)_2$ (1.0 mmol) and LiCl (5.0 mmol) in dimethylformamide (3 ml), aryl iodide (1.0 mmol) and allyl trimethylsilyl ether (1.0 mmol) were added under a nitrogen atmosphere, and then the reaction mixture was stirred at 110°C for 5-15h. After cooling, ether (10 ml) was added and the precipitate was removed by filtration. The products were isolated by column chromatography on silica gel from the filtrate.

Results are summarized in Table 1. When LiCl was not added, no α,β-unsaturated carbonyl compounds were formed, and palladium metal was deposited. The use of 5 equiv. of LiCl afforded a higher yield than in the case of 2 or 10 equiv. Cupric chloride and sodium carbonate were less effective than LiCl.[2] Dimethylformamide was more suitable as a solvent than acetonitrile. In the preparation of α,β-unsaturated ketones, a substantial amount of the saturated ketone was produced. The reason for this variation has not been determined. The arylation occurred selectively at the 3-position of allylic alcohols, although in most of the palladium-catalyzed reaction of allylic alcohols with aryl halides, products are contaminated with α-aryl carbonyl compounds.[1] It should be noted that the present reaction proceeds stereoselectively. Only (E)-α,β-unsaturated carbonyl compounds were obtained without the formation of Z-isomers. The products, 2a and 2b, might be possible in the reaction of iodobenzene with the silyl ether of methallyl alcohol (1a), but no α-benzyl acrolein (2a) was detected as a product.

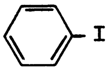
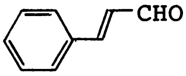
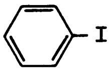
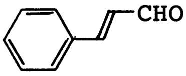
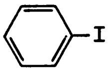
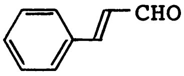
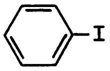
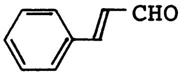
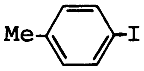
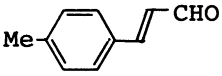
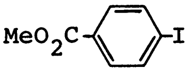
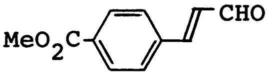
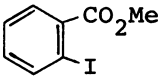
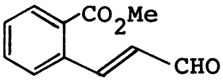
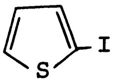
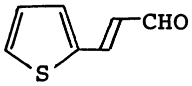
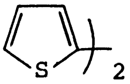
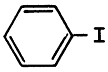
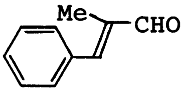
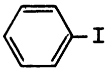
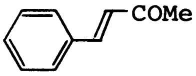
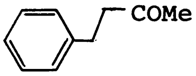
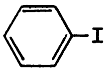
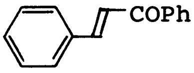
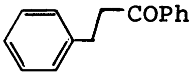


When 1b was treated with Pd(OAc)$_2$ and LiCl, no cinnamaldehyde was detected.



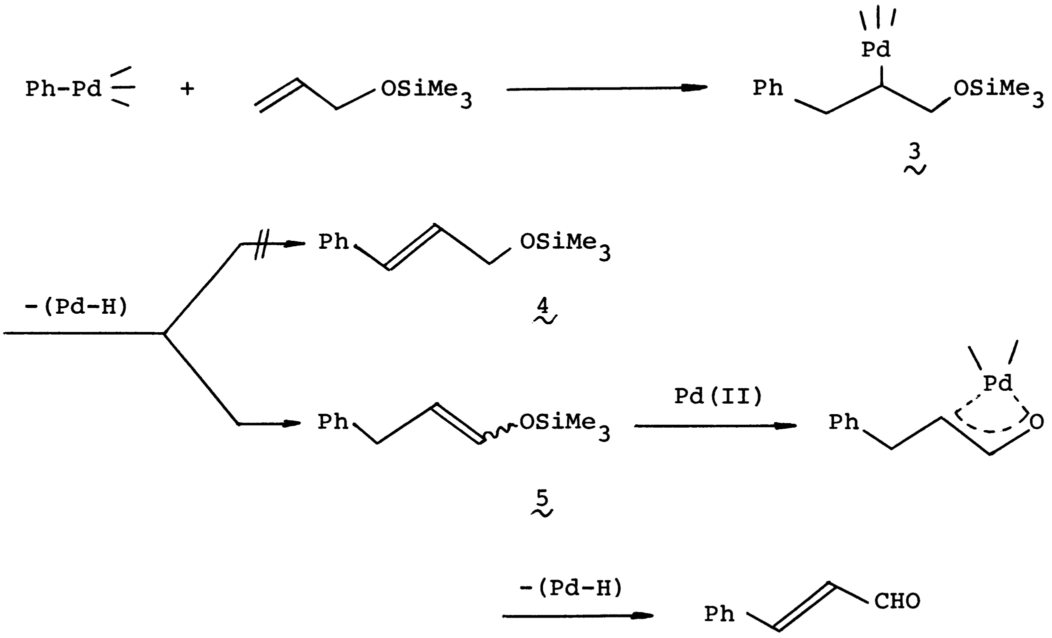
From these results, Scheme 1 may be a possible reaction path. The complex 3, which is obtained by regiospecific addition of a phenylpalladium complex to the allylic double bond, undergoes β-elimination of a Pd-H species to afford selectively the enol ether 5 but not the allyl ether 4. A palladium(II) catalyst induces dehydrosilylation of the enol ether 5 to give trans-cinnamaldehyde. It is well known that silyl enol ethers are subject to palladium-assisted dehydrosilylation to give (E)-α,β-unsaturated carbonyl compounds via oxo-π-allylpalladium complex intermediates.[3] The enol ether 5 (E and Z mixture) was converted to trans-cinnamaldehyde in 91% yield by treating with Pd(OAc)$_2$ and LiCl in dimethylformamide at 110°C for 2 h.

Table 1 Reaction of Allyl Silyl Ether with Aryl Iodide

ArI	**1**		Salt(equiv.)	Solv.	Reaction		Product (%)[a)]	
	R^1	R^2			°C	h		
	H	H	LiCl (5.0)	DMF	110	7		(70)
	H	H	$CuCl_2$ (2.5)	DMF	110	15		(5)
	H	H	LiCl (5.0)	MeCN	82	28		(40)
	H	H	Na_2CO_3 (5.0)	MeCN	82	14		(20)
	H	H	LiCl (5.0)	DMF	110	7		(40)
	H	H	LiCl (5.0)	DMF	110	8		(18)
	H	H	LiCl (5.0)	DMF	110	7		(33)
	H	H	LiCl (5.0)	DMF	110	5		(30)
							+ 	(26)
	Me	H	LiCl (5.0)	DMF	110	8		(40)
	H	Me	LiCl (5.0)	DMF	110	10		(40)
							+ 	(42)
	H	Ph	LiCl (5.0)	DMF	110	15		(23)
							+ 	(47)

a) Yields were determined by GLC.

Scheme 1



References and Note

1. J. B. Melpolder and R. F. Heck, J. Org. Chem., 41, 265 (1976).
A. J. Chalk and S. A. Magennis, ibid., 41, 273, 1206 (1976).
Y. Tamaru, Y. Yamada and Z. Yoshida, ibid., 43, 3396 (1978).

2. It was clarified that the reaction did not proceed catalytically even if an additive such as triethylamine or cupric salt was added.

3. Y. Ito, T. Hirao and T. Saegusa, J. Org. Chem., 43, 1011 (1978).
Y. Ito, H. Aoyama, T. Hirao, A. Mochizuki and T. Saegusa, J. Am. Chem. Soc., 101, 494 (1979).

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