

Barbier-type Carbonyl-allylation with Allyl Compounds and SnCl₂ in the Presence of PdCl₂[PPh₂(*m*-C₆H₄SO₃Na)]₂ under Two-phase Conditions

Tamon Okano,* Jitsuo Kiji, and Takanori Doi

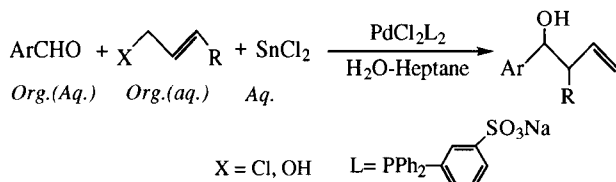
Department of Materials Science, Faculty of Engineering, Tottori University, Tottori 680

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The hydrophilic palladium complex efficiently catalyzes the allylation of carbonyl compounds with allyl chlorides or allyl alcohols and SnCl₂ under aqueous-organic biphasic conditions, which allow us easily to separate the product and to recover the organic solvent from the reaction mixture.

The palladium-catalyzed allylation of aldehydes with allyl compounds and SnCl₂ in DMF or DMSO is synthetically an important reaction.¹ However, the use of amphiphilic solvents makes the separation of product difficult, and pollutes the aqueous drainage. The reaction is very slow under liquid-solid biphasic conditions.² Recently, hydrophilic transition metal catalysts have been reported to be effective for biphasic reactions.³ We have also found that some of the hydrophilic metal complexes act as counter phase transfer catalyst which has concerted double functions as a transition metal catalyst and as an inverse phase transfer catalyst able to transport lipophilic molecules from organic phase into aqueous phase.⁴ Therefore we investigated the biphasic carbonyl-allylation using a hydrophilic catalyst.

The allylation of benzaldehyde with allyl chlorides and SnCl₂ smoothly proceeded in the presence of hydrophilic complex, PdCl₂[PPh₂(*m*-C₆H₄SO₃Na)]₂ (**1**), under aqueous-organic biphasic conditions (see Table 1). The allylation required excess uses of allyl chloride and SnCl₂. The use of stoichiometric amounts of these reduced the yield. Compared to the homogeneous allylation using amphiphilic solvents, the products



were easily and economically isolated in this biphasic reaction, since the organic layer which contains the products and the volatile and inexpensive solvents was easily separated from the aqueous layer containing the catalyst and tin compounds.

The biphasic allylation with allyl alcohol which is water-soluble was similarly achieved. Not only lipophilic aldehydes, sodium *p*-benzaldehydesulfonate was also allylated with either allyl chloride or allyl alcohol under the biphasic conditions. However, hydrophobic catalyst, PdCl₂{P(*p*-C₆H₄CH₃)₃}₂ (**2**), exhibited a poor reactivity in these biphasic reactions. Since the steric and electronic effects of the hydrophobic phosphine differ little from those of the hydrophilic phosphine, the high efficiency of **1** is

Table 1. Palladium-catalyzed allylation of aldehydes with allyl compounds and SnCl₂ under biphasic conditions^a

Catalyst	Aldehyde	Allyl compound	Yield/% ^b
1	PhCHO	CH ₂ =CHCH ₂ Cl	98
1	PhCHO ^c	CH ₂ =CHCH ₂ Cl	93
1	PhCHO ^d	CH ₂ =CHCH ₂ Cl	84
1	PhCHO	(E)-CH ₃ CH=CHCH ₂ Cl	91 ^e
1	PhCHO ^c	(E)-CH ₃ CH=CHCH ₂ Cl	48 ^e
1	PhCHO ^d	(E)-CH ₃ CH=CHCH ₂ Cl	31 ^f
1	PhCHO	CH ₂ =CHCH ₂ OH	98
1	<i>o</i> -NaO ₃ SC ₆ H ₄ CHO	CH ₂ =CHCH ₂ Cl	95
1	<i>o</i> -NaO ₃ SC ₆ H ₄ CHO	CH ₂ =CHCH ₂ OH	93
2	PhCHO	CH ₂ =CHCH ₂ OH	5
2	PhCHO	CH ₂ =CHCH ₂ OH	17
2	<i>o</i> -NaO ₃ SC ₆ H ₄ CHO	CH ₂ =CHCH ₂ Cl	16
2	<i>o</i> -NaO ₃ SC ₆ H ₄ CHO	CH ₂ =CHCH ₂ OH	8

^aA mixture of ArCHO (10 mmol), allyl compound (20 mmol), SnCl₂ (30 mmol), palladium catalyst (0.1 mmol) in a solution of heptane (10 cm³) and H₂O (10 cm³) was vigorously stirred for 7 h at 35 °C. ^bThe yield of allylated products was determined by GLC (OV17, 30m) using internal standards. ^cToluene was used instead of heptane. ^dAnisole was used instead of heptane. ^eSyn:anti=2:8. ^fSyn:anti:5-phenyl-5-hydroxy-2-pentene=1:3:1.

Table 2. Consumption rate of allyl chloride^a

Catalyst	SnCl ₂ /mmol	Time/h	Consumption/% ^b
1	30	2	36
1	40	2	75
2	30	2	4
2	40	2	5
none	30	20	1

^aA mixture of allyl compound (20 mmol), SnCl₂ and catalyst (0.1 mmol) in heptane (10 cm³) and H₂O (10 cm³) was vigorously stirred at 35 °C. ^bThe consumption of allyl chloride in the heptane layer was determined by GLC (OV17, 30m) using benzene as an internal standard.

probably ascribed to the hydrophilicity.

Interestingly, the biphasic allylation with allyl chlorides in the presence of **1** was faster in heptane than in toluene or anisole. Analogous solvent effects have been observed in the counter phase transfer reactions,⁴ suggesting that the allylation involves the counter phase transfer step. One of the palladium-demanded

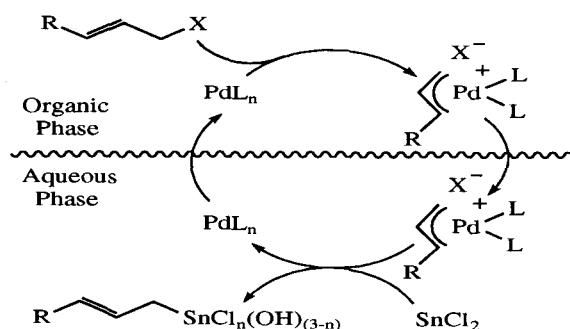


Figure 1. Proposed mechanism for the counter phase transfer step of the biphasic allylation.

Table 3. Biphasic allylation of carbonyl compounds^a

Carbonyl compound	Allyl compound	Time/h	Yield/% ^b
CH ₃ CHO ^c	CH ₂ =CHCH ₂ Cl	50	89
(CH ₃) ₂ CHCHO	CH ₂ =CHCH ₂ Cl	7	98 (83)
PhCH ₂ CH ₂ CHO	CH ₂ =CHCH ₂ Cl	7	98 (91)
<i>p</i> -CH ₃ OOC-C ₆ H ₄ CHO	CH ₂ =CHCH ₂ Cl	10	97 (75)
<i>p</i> -NCC ₆ H ₄ CHO	CH ₂ =CHCH ₂ Cl	10	98 (88)
Cyclohexanone	CH ₂ =CHCH ₂ Cl	50	87
(CH ₃ CH ₂) ₂ CO	CH ₂ =CHCH ₂ Cl	24	32
PhCHO	CH ₂ =C(CH ₃)CH ₂ Cl	40	95
PhCHO	(E)-CH ₃ CH ₂ =CHCH ₂ OH	70	97 (89) ^d
PhCHO	(E)- <i>n</i> -PrCH ₂ =CHCH ₂ Cl	50	94 ^e
PhCHO	(E)- <i>n</i> -PrCH ₂ =CHCH ₂ OH	70	96 ^e
PhCHO ^f	CH ₂ =CHCH ₂ OAc	7	98
PhCHO ^f	CH ₂ =CHCH ₂ OPh	7	2

^aA mixture of carbonyl compound (10 mmol), allyl compound (20 mmol), SnCl₂ (30 mmol) and **1** (0.1 mmol) in H₂O (10 cm³) and heptane (10 cm³) was vigorously stirred at 35 °C.

^bThe yield of allylated products was determined by GLC (OV17, 30m) using internal standards, and the isolated yield is shown in parentheses. ^cAt 30 °C. ^dSyn:anti=3:7. ^eThe diastereomeric ratio was not determined. ^fAt 60 °C.

steps is the reaction of allyl compounds with SnCl₂ to form allylstannic compounds. In the absence of aldehyde, the consumption rate of allylchloride in the heptane phase was much

faster in the reaction with **1** than with **2** (see Table 2). This result suggests that the hydrophilic catalyst efficiently transports allyl chloride from the organic phase via hydrophilic π-allyl palladium species into the aqueous phase in which SnCl₂ exists.

The biphasic allylation with **1** was applicable to aliphatic aldehydes as well as aromatic aldehydes, and gave the allylated products in good yields (see Table 3). The reactivity of aldehydes was little affected by their lipophilicity, while the allyl compounds having lipophilic substituents slowly reacted. Cyano and ester groups were not affected in this reaction. Ketones were also allylated, though the reactions were slow compared with aldehydes. Thus the applicability of the biphasic reaction is roughly equivalent to that of the homogeneous allylation in amphiphilic solvents. The selectivities of homogeneous reaction with 2-butenyl compounds strongly depend on the solvents. In the biphasic reaction, the 2-butenyl derivatives selectively underwent γ-addition, and dominantly gave the anti isomers. These regio- and diastereo-selectivities were considerably high, and were comparable to those of the homogeneous reaction in the presence of large amounts of water.

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