Barbier-type Carbonyl-allylation with Allyl Compounds and $SnCl_2$ in the Presence of $PdCl_2[PPh_2(m\text{-}C_6H_4SO_3Na)]_2$ under Two-phase Conditions

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The hydrophilic palladium complex efficiently catalyzes the allylation of carbonyl compounds with allyl chlorides or allyl alcohols and $SnCl_2$ under aqueous-organic biphase 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 $SnCl_2$ 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 biphase 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 liphophilic 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 $SnCl_2$ smoothly proceeded in the presence of hydrophilic complex, $PdCl_2[PPh_2(m\text{-}C_6H_4SO_3Na)]_2$ (**1**), under aqueous-organic biphase conditions (see Table 1). The allylation required excess uses of allyl chloride and $SnCl_2$. 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.

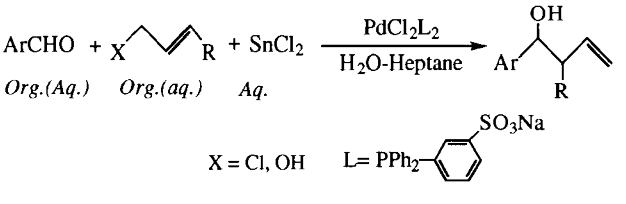

Table 1. Palladium-catalyzed allylation of aldehydes with allyl compounds and $SnCl_2$ under biphasic conditions[a]

Catalyst	Aldehyde	Allyl compound	Yield/%[b]
1	PhCHO	$CH_2{=}CHCH_2Cl$	98
1	PhCHO[c]	$CH_2{=}CHCH_2Cl$	93
1	PhCHO[d]	$CH_2{=}CHCH_2Cl$	84
1	PhCHO	(E)-$CH_3CH{=}CHCH_2Cl$	91[e]
1	PhCHO[c]	(E)-$CH_3CH{=}CHCH_2Cl$	48[e]
1	PhCHO[d]	(E)-$CH_3CH{=}CHCH_2Cl$	31[f]
1	PhCHO	$CH_2{=}CHCH_2OH$	98
1	o-$NaO_3SC_6H_4CHO$	$CH_2{=}CHCH_2Cl$	95
1	o-$NaO_3SC_6H_4CHO$	$CH_2{=}CHCH_2OH$	93
2	PhCHO	$CH_2{=}CHCH_2OH$	5
2	PhCHO	$CH_2{=}CHCH_2OH$	17
2	o-$NaO_3SC_6H_4CHO$	$CH_2{=}CHCH_2Cl$	16
2	o-$NaO_3SC_6H_4CHO$	$CH_2{=}CHCH_2OH$	8

[a] A mixture of ArCHO (10 mmol), allyl compound (20 mmol), $SnCl_2$ (30 mmol), palladium catalyst (0.1 mmol) in a solution of heptane (10 cm^3) and H_2O (10 cm^3) was vigorously stirred for 7 h at 35 °C. [b] The yield of allylated products was determined by GLC (OV17, 30m) using internal standards. [c] Toluene was used instead of heptane. [d] Anisole was used instead of heptane. [e] Syn:anti=2:8. [f] Syn: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

[a] A mixture of allyl compound (20 mmol), $SnCl_2$ and catalyst (0.1 mmol) in heptane (10 cm^3) and H_2O (10 cm^3) was vigorously stirred at 35 °C. [b] The consumption of allyl chloride in the heptane layer was determined by GLC (OV17, 30m) using benzene as an internal standard.

The biphasic allylation with allyl alcohol which is water-soluble was similarly achieved. Not only lipophilic aldehydes, sodium p-benzaldehydesufonate was also allylated with either allyl chloride or allyl alcohol under the biphasic conditions. However, hydrophobic catalyst, $PdCl_2\{P(p\text{-}C_6H_4CH_3)_3\}_2$ (**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 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

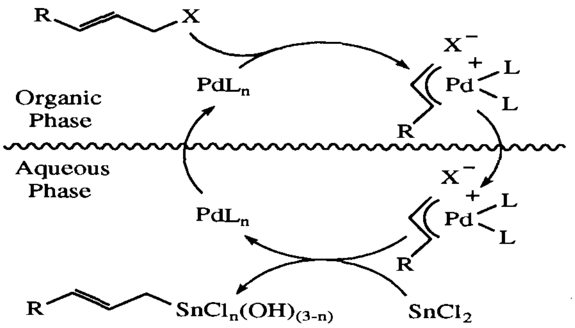

Figure 1. Proposed mechanism for the counter phase transfer step of the biphasic allylation.

Table 3. Biphasic allylation of carbonyl compounds[a]

Carbonyl compound	Allyl compound	Time/h	Yield/%[b]
CH_3CHO[c]	$CH_2{=}CHCH_2Cl$	50	89
$(CH_3)_2CHCHO$	$CH_2{=}CHCH_2Cl$	7	98 (83)
$PhCH_2CH_2CHO$	$CH_2{=}CHCH_2Cl$	7	98 (91)
p-$CH_3OOCC_6H_4CHO$	$CH_2{=}CHCH_2Cl$	10	97 (75)
p-NCC_6H_4CHO	$CH_2{=}CHCH_2Cl$	10	98 (88)
Cyclohexanone	$CH_2{=}CHCH_2Cl$	50	87
$(CH_3CH_2)_2CO$	$CH_2{=}CHCH_2Cl$	24	32
PhCHO	$CH_2{=}C(CH_3)CH_2Cl$	40	95
PhCHO	(E)-$CH_3CH_2{=}CHCH_2OH$	70	97 (89)[d]
PhCHO	(E)-*n*-$PrCH_2{=}CHCH_2Cl$	50	94[e]
PhCHO	(E)-*n*-$PrCH_2{=}CHCH_2OH$	70	96[e]
PhCHO[f]	$CH_2{=}CHCH_2OAc$	7	98
PhCHO[f]	$CH_2{=}CHCH_2OPh$	7	2

[a] A mixture of carbonyl compound (10 mmol), allyl compound (20 mmol), $SnCl_2$ (30 mmol) and 1 (0.1 mmol) in H_2O (10 cm^3) and heptane (10 cm^3) was vigorously stirred at 35 °C. [b] The yield of allylated products was determined by GLC (OV17, 30m) using internal standards, and the isolated yield is shown in parentheses. [c] At 30 °C. [d] Syn:anti=3:7. [e] The diastereomeric ratio was not determined. [f] At 60 °C.

steps is the reaction of allyl compounds with $SnCl_2$ to form allylstannic compounds. In the absence of aldehyde, the consumption rate of allyl chloride 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 $SnCl_2$ 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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