

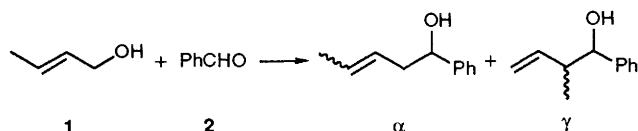
Ultrasound-promoted Carbonyl Allylation by Allylic Alcohols with Palladium–Tin Dichloride in Nonpolar Solvents: Inversed Regiocontrol of Carbonyl Allylation in Polar Solvents

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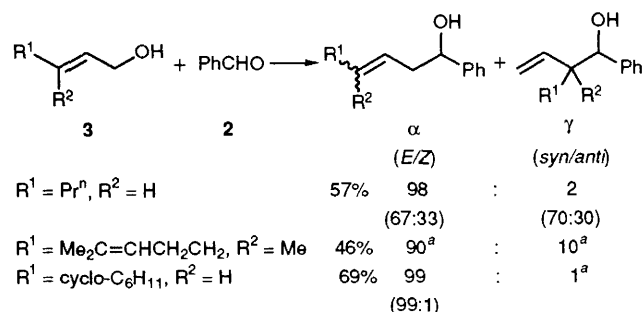
Heterogeneous carbonyl allylation by γ -substituted allylic alcohols with Pd–SnCl₂ in a nonpolar solvent such as diethyl ether was promoted by ultrasound to cause α -addition, with a regioselectivity which is the inverse of that in homogeneous carbonyl allylation in polar solvents such as dimethylformamide, 1,3-dimethylimidazolidin-2-one and tetrahydrofuran–H₂O.

Ultrasound activates metals such as lithium, magnesium, aluminium, zinc *etc.*, accelerating their organometallic reactions.¹ We have previously reported carbonyl allylation by allylic alcohols with Pd–SnCl₂ in polar solvents such as tetrahydrofuran (THF), dimethylformamide (DMF), 1,3-dimethylimidazolidin-2-one (DMI) and dimethyl sulfoxide (DMSO), which dissolve SnCl₂.² The heterogeneous carbonyl allylation by (*E*)-but-2-en-1-ol **1** with Pd–SnCl₂ proceeds extremely slowly at ambient temperature in nonpolar solvents such as diethyl ether, dichloromethane and chloroform leading to α -addition, with a regioselectivity which is the inverse of that in homogeneous carbonyl allylation in polar solvents. We here report that heterogeneous carbonyl allylation by γ -substituted allylic alcohols with Pd–SnCl₂ in nonpolar solvents is promoted by ultrasound to cause α -regioselective addition.³



Scheme 1 Conditions: PdCl₂(PhCN)₂, SnCl₂, 10–15 °C, ultrasonication

Acceleration of reactions by ultrasound and regioselectivity (α - or γ -addition) were investigated in the allylation of benzaldehyde **2** by **1** with PdCl₂(PhCN)₂–SnCl₂ in nonpolar solvents (Scheme 1). The results are summarized in Table 1. Ultrasonication for 4 h in diethyl ether led to the highest yield without much lowering of α -selectivity (entries 4 and 5). The reaction did not proceed in hexane, benzene or toluene. Reactions in mixed solvents gave low yields but high α -selectivity (entries 8–10). Yield and α -selectivity were inversely affected by changes in the ratio of **1** to **2** in Et₂O; 20% yield,



Scheme 2 Conditions: PdCl₂(PhCN)₂, SnCl₂, 10–15 °C, ultrasonication; 4 h; room temp., 48 h. ^a The ratio of stereoisomers (*E/Z* or *syn/anti*) was not confirmed.

Table 1 Ultrasound-promoted allylation of **2** by **1** with Pd-SnCl₂^a

Entry	Solvent	Time/h ^b	Yield (%) ^c	α (E:Z)	:	γ ^d (syn:anti)
1	Et ₂ O	0 ^e	8	92 (62:38)	:	8 (54:46)
2	Et ₂ O	2	17	82 (84:16)	:	18 (82:18)
3	Et ₂ O	2 ^f	38	83 (79:21)	:	17 (82:18)
4	Et ₂ O	4	56	78 (79:21)	:	22 (82:18)
5	Et ₂ O	4 ^f	76	75 (88:12)	:	25 (66:34)
6	Et ₂ O	8	46	80 (76:24)	:	20 (75:25)
7	Et ₂ O	8 ^f	44	81 (72:25)	:	19 (72:28)
8	Et ₂ O-hexane (1:1)	4	15	79 (83:17)	:	21 (70:30)
9	Et ₂ O-benzene (1:1)	4	23	92 (73:27)	:	8 (77:23)
10	Et ₂ O-toluene (4:1)	4	34	92 (74:26)	:	8 (67:33)

^a Ultrasound-promoted carbonyl allylation was carried out using **1** (3 mmol), **2** (1 mmol), PdCl₂(PhCN)₂ (0.02 mmol), and SnCl₂ (6 mmol) in solvent (5 ml) at 10–15 °C. ^b Ultrasonication time. ^c Isolated yield. ^d The ratio was determined by 270 MHz ¹H NMR (Jeol GX-270) and capillary GC (PEG20M, 0.25 mm × 30 m). ^e The reaction mixture was stirred at ambient temperature for 72 h. ^f After irradiation without **2** followed by addition of **2**, the reaction mixture was stirred at ambient temperature for 24 h.

α:γ 96:4 with **1** + **2** in 1:2 ratio; 68% yield, α:γ 66:34 with **1** + **2** in 5:1 ratio.

Allylic alcohols with a more bulky substituent than methyl at the γ-position showed high α-selectivity under the same conditions as those of entry 5 in Table 1, as shown in Scheme 2. The addition to benzaldehyde of allylic alcohols bearing one or two substituents in the α-position, such as but-3-en-2-ol and linalool, afforded products (>96% regioselectivity) analogous to the α-adducts shown in Scheme 1 or 2 in low yields (10–15%).

The ultrasound-promoted carbonyl allylation by γ-substituted allylic alcohols in nonpolar solvents thus leads to α-addition, the inverse of that in carbonyl allylation in polar solvents.

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