# Palladium-catalysed Carbonyl Allylation by Isoprene *via* Regioselective 1,4-Addition of Tin Hydride formed *in situ*

### Yoshiro Masuyama,\* Megumi Tsunoda and Yasuhiko Kurusu

Department of Chemistry, Sophia University 7-1 Kioicho, Chiyoda-ku, Tokyo 102, Japan

Isoprene reacts with aldehydes in the presence of a catalytic amount of  $Pd(OAc)_2$ –4PPh<sub>3</sub> or  $Pd(PPh_3)_4$  and a stoichiometric amount of  $SnCl_2$  at 40–50 °C in AcOH–H<sub>2</sub>O to produce 1-substituted 2,2-dimethyl-3-buten-1-ols regioselectively.

Allylic alcohols and esters can be applied to palladiumcatalysed carbonyl allylation with SnCl<sub>2</sub>, in which the formation of a  $\pi$ -allylpalladium complex followed by that of an allylic tin compound are the key steps.<sup>1</sup> Any substrate, transformed into a  $\pi$ -allylpalladium complex, could be utilized for palladium-catalysed carbonyl allylation with SnCl<sub>2</sub>. Here we report the transformation of isoprene into a  $\pi$ -allylpalladium complex<sup>2</sup> and its application to carbonyl allylation with SnCl<sub>2</sub>.<sup>3</sup>

Using benzaldehyde 2a and octanal 2b, we investigated palladium-catalysed carbonyl allylation by isoprene 1 with SnCl<sub>2</sub> under various conditions, as summarized in Table 1 [eqn. (1)]. Using Pd(OAc)<sub>2</sub> as a catalyst and PPh<sub>3</sub> as a ligand at 40 °C for 24 h in H<sub>2</sub>O-HOAc under an argon atmosphere, 2,2-dimethyl-1-phenyl-3-buten-1-ol **3a** was regioselectively formed from the allylation of **2a** by 1 (entry 1). No reaction occurred at 25 °C. Prolonged heating lowered the yield of **3a** 

Table 1 Palladium-catalysed allylation of 2a and 2b by 1 with  $SnCl_2^a$ 

Entry	Aldehyde	Ligand/mmol	T/⁰C	<i>t/</i> h	Yield <sup>b</sup> (%)
1	2a	PPh <sub>3</sub> /0.08	40	24	85
2	2a	PPh <sub>3</sub> /0.08	40	72	72
3	2a	PPh <sub>3</sub> /0.08	40	120	43
4	2a	PPh <sub>3</sub> /0.08	55	72	29
5	2a	PPh <sub>3</sub> /0.04	40	24	67
6	2b	PPh <sub>3</sub> /0.08	40	24	23
7	2b	PPh <sub>3</sub> /0.08	50	24	29
8	2b	PPh <sub>3</sub> /0.08	80	6	34c
9	2b		50	24	32c,d
10	2b	PPh <sub>3</sub> /0.02	50	24	43c,d
11	2b	PPh <sub>3</sub> /0.08	50	24	39 <sup>d</sup>

<sup>*a*</sup> The allylation of benzaldehyde or octanal (1 mmol) by isoprene (5 mmol) was carried out with Pd(OAc)<sub>2</sub> (0.02 mmol) and SnCl<sub>2</sub> (2 mmol) in H<sub>2</sub>O (1 ml) and AcOH (2 ml). <sup>*b*</sup> Isolated yields. <sup>*c*</sup> The regioisomer, 2-methyl-2-dodecen-5-ol was obtained in 8–10% yields. <sup>*d*</sup> Pd(PPh<sub>3</sub>)<sub>4</sub> was used as a catalyst.

Table 2 Palladium-catalysed allylation of various aldehydes RCHO by 1 with  $SnCl_{2^{n}}$ 

]	Entry	Aldehyde R	Catalyst	Yield <sup>b</sup> (%)
	1 2 3 4 5 6	$4-NCC_{6}H_{4}$ $4-MeO_{2}CC_{6}H_{4}$ $2-BrC_{6}H_{4}$ $4-ClC_{6}H_{4}$ $4-ClC_{6}H_{4}$ $4-MeOC_{6}H_{4}$ $PhCH_{2}CH_{2}$	$Pd(OAc)_2$ $Pd(PPh_3)_4$ $Pd(PPh_3)_4$ $Pd(OAc)_2$ $Pd(OAc)_2$ $Pd(OAc)_2$ $Pd(OAc)_2$	61 82 57 58 46 <sup>c</sup> 31
2	7 8 9	$n-C_{10}H_{21}$ CH <sub>2</sub> =CH(CH <sub>2</sub> ) <sub>8</sub> $c-C_6H_{11}$	$Pd(PPh_3)_4$ $Pd(PPh_3)_4$ $Pd(PPh_3)_4$ $Pd(PPh_3)_4$	35d 32d 17d

<sup>*a*</sup> The allylation of aldehyde (1 mmol) by isoprene (5 mmol) was carried out with Pd catalyst (0.02 mmol), PPh<sub>3</sub> (0.08 mmol), and SnCl<sub>2</sub> (2 mmol) at 40 °C for 24 h in H<sub>2</sub>O (1 ml) and AcOH (2 ml). <sup>*b*</sup> Isolated yields. <sup>*c*</sup> The reaction was carried out at 80 °C for 2 h. <sup>*d*</sup> The reaction was carried out with PPh<sub>3</sub> (0.04 mmol) at 50 °C. The regioisomers, 1-substituted 4-methylpent-3-en-1-ols, were obtained in 6–11% yields.

(entries 2-4). The use of ligands such as PBu<sub>3</sub>, P(OMe)<sub>3</sub>, P(o-tolyl)<sub>3</sub>, dppe, and AsPh<sub>3</sub> lowered the yields (45-59%). Neither THF-HOAc nor DMF-HOAc can be used as solvents for the allylation. The allylation of an aliphatic aldehyde, octanal 2b, by 1 did not proceed as smoothly under the same conditions as with 2a (entry 6). Raising the temperature promotes the allylation of 2b, enhancing the yield of 3,3dimethyl-1-undecen-4-ol 3b while lowering the regioselectivity (entry 8). Pd(PPh<sub>3</sub>)<sub>4</sub> with extra PPh<sub>3</sub> was a better catalyst than Pd(OAc)<sub>2</sub>-4PPh<sub>3</sub> in the allylation of **2b** at 50 °C (entries 7 and 9-11). Methanesulfonic acid (2 mmol) (or toluene-psulfonic acid) instead of acetic acid caused the allylation of  $\mathbf{\hat{2}b}$ in THF to give 3b in 24% (12%) yield. Palladium-catalysed allylation of various aldehydes by 1 with SnCl<sub>2</sub> proceeded under the same conditions as with 2a and 2b to give 1-substituted 2,2-dimethyl-3-buten-1-ols. Representative results are summarized in Table 2. Aromatic aldehydes bearing either an electron-withdrawing group or an electrondonating group can be used in the allylation (entries 1-5). Non-bulky aliphatic aldehydes exhibited almost the same reactivity as that of 2b (entries 6-8). Both reactivity and selectivity are low in the allylation of a bulky aldehyde, cyclohexanecarbaldehyde (entry 9).

Since 1-substituted 2,2-dimethyl-3-buten-1-ols have been regioselectively produced in all cases, 3-methyl-2-butenyltin intermediate **D**, derived from isoprene with Pd/SnCl<sub>2</sub>/HOAc, probably attacks aldehydes at the  $\gamma$ -position similarly to palladium-catalysed carbonyl allylation by allylic alcohols with SnCl<sub>2</sub>, as shown in Scheme 1.<sup>1</sup> The allyltin intermediate **D** is probably formed *via* the formation of isoprene coordinated stannylpalladium hydride **A** followed by (*a*) insertion of



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monosubstituted olefin to the Pd–Sn bond (the formation of  $\pi$ -allylpalladium hydride **B**)<sup>4</sup> or (b) insertion of disubstituted olefin to the Pd–H bond (the formation of  $\pi$ -allylpalladium stannate **C**).<sup>5</sup>

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