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

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Isoprene reacts with aldehydes in the presence of a catalytic amount of $Pd(OAc)_2$–$4PPh_3$ or $Pd(PPh_3)_4$ and a stoichiometric amount of $SnCl_2$ at 40–50 °C in $AcOH$–H_2O to produce 1-substituted 2,2-dimethyl-3-buten-1-ols regioselectively.

Allylic alcohols and esters can be applied to palladium-catalysed carbonyl allylation with $SnCl_2$, in which the formation of a π-allylpalladium complex followed by that of an allylic tin compound are the key steps.[1] Any substrate, transformed into a π-allylpalladium complex, could be utilized for palladium-catalysed carbonyl allylation with $SnCl_2$. Here we report the transformation of isoprene into a π-allylpalladium complex[2] and its application to carbonyl allylation with $SnCl_2$.[3]

Using benzaldehyde **2a** and octanal **2b**, we investigated palladium-catalysed carbonyl allylation by isoprene **1** with $SnCl_2$ under various conditions, as summarized in Table 1 [eqn. (1)]. Using $Pd(OAc)_2$ as a catalyst and PPh_3 as a ligand at 40 °C for 24 h in H_2O–$HOAc$ 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** (entries 2–4). The use of ligands such as PBu_3, $P(OMe)_3$, $P(o\text{-tolyl})_3$, dppe, and $AsPh_3$ 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 3,3-dimethyl-1-undecen-4-ol **3b** while lowering the regioselectivity (entry 8). $Pd(PPh_3)_4$ with extra PPh_3 was a better catalyst than $Pd(OAc)_2$–$4PPh_3$ in the allylation of **2b** at 50 °C (entries 7 and 9–11). Methanesulfonic acid (2 mmol) (or toluene-*p*-sulfonic acid) instead of acetic acid caused the allylation of **2b** in THF to give **3b** in 24% (12%) yield. Palladium-catalysed allylation of various aldehydes by **1** with $SnCl_2$ 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 electron-donating 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 $Pd/SnCl_2/HOAc$, probably attacks aldehydes at the γ-position similarly to palladium-catalysed carbonyl allylation by allylic alcohols with $SnCl_2$, as shown in Scheme 1.[1] The allyltin intermediate **D** is probably formed *via* the formation of isoprene coordinated stannylpalladium hydride **A** followed by (*a*) insertion of

Table 1 Palladium-catalysed allylation of **2a** and **2b** by **1** with $SnCl_2$[a]

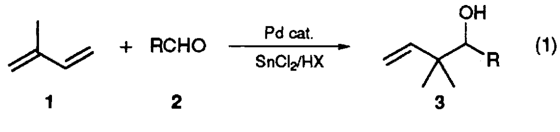
Entry	Aldehyde	Ligand/mmol	*T*/°C	*t*/h	Yield[b] (%)
1	**2a**	PPh_3/0.08	40	24	85
2	**2a**	PPh_3/0.08	40	72	72
3	**2a**	PPh_3/0.08	40	120	43
4	**2a**	PPh_3/0.08	55	72	29
5	**2a**	PPh_3/0.04	40	24	67
6	**2b**	PPh_3/0.08	40	24	23
7	**2b**	PPh_3/0.08	50	24	29
8	**2b**	PPh_3/0.08	80	6	34[c]
9	**2b**	—	50	24	32[c,d]
10	**2b**	PPh_3/0.02	50	24	43[c,d]
11	**2b**	PPh_3/0.08	50	24	39[d]

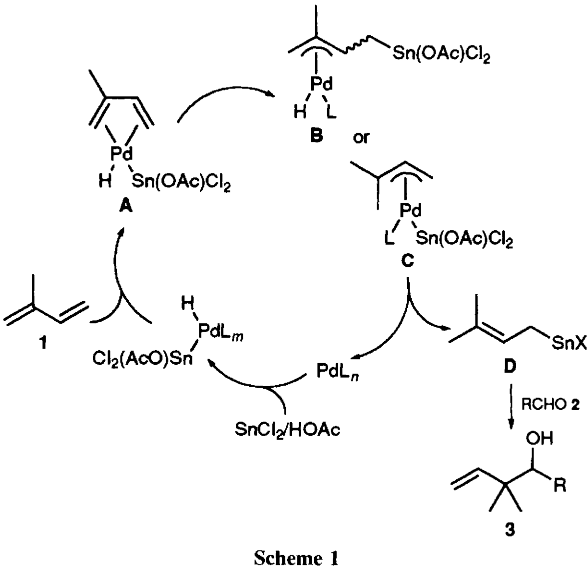
[a] The allylation of benzaldehyde or octanal (1 mmol) by isoprene (5 mmol) was carried out with $Pd(OAc)_2$ (0.02 mmol) and $SnCl_2$ (2 mmol) in H_2O (1 ml) and AcOH (2 ml). [b] Isolated yields. [c] The regioisomer, 2-methyl-2-dodecen-5-ol was obtained in 8–10% yields. [d] $Pd(PPh_3)_4$ was used as a catalyst.

Table 2 Palladium-catalysed allylation of various aldehydes RCHO by **1** with $SnCl_2$[a]

Entry	Aldehyde R	Catalyst	Yield[b] (%)
1	4-NCC_6H_4	$Pd(OAc)_2$	61
2	$4\text{-MeO}_2CC_6H_4$	$Pd(PPh_3)_4$	82
3	2-BrC_6H_4	$Pd(PPh_3)_4$	57
4	4-ClC_6H_4	$Pd(OAc)_2$	58
5	4-MeOC_6H_4	$Pd(OAc)_2$	46[c]
6	$PhCH_2CH_2$	$Pd(OAc)_2$	31
7	$n\text{-}C_{10}H_{21}$	$Pd(PPh_3)_4$	35[d]
8	$CH_2{=}CH(CH_2)_8$	$Pd(PPh_3)_4$	32[d]
9	$c\text{-}C_6H_{11}$	$Pd(PPh_3)_4$	17[d]

[a] The allylation of aldehyde (1 mmol) by isoprene (5 mmol) was carried out with Pd catalyst (0.02 mmol), PPh_3 (0.08 mmol), and $SnCl_2$ (2 mmol) at 40 °C for 24 h in H_2O (1 ml) and AcOH (2 ml). [b] Isolated yields. [c] The reaction was carried out at 80 °C for 2 h. [d] The reaction was carried out with PPh_3 (0.04 mmol) at 50 °C. The regioisomers, 1-substituted 4-methylpent-3-en-1-ols, were obtained in 6–11% yields.





Scheme 1

monosubstituted olefin to the Pd–Sn bond (the formation of π-allylpalladium hydride **B**)[4] or (*b*) insertion of disubstituted olefin to the Pd–H bond (the formation of π-allylpalladium stannate **C**).[5]

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