Palladium-catalysed carbonyl allylation by 2-methylenepropane-1,3-diol

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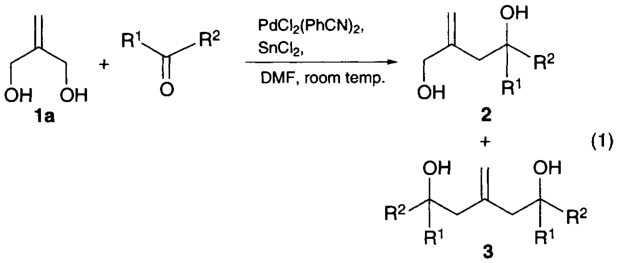
2-Methylenepropane-1,3-diol first allylates an aldehyde exclusively at the allylic alcohol moiety at room temperature and then, at 50 °C, allylates another aldehyde also at the allylic alcohol moiety, in the presence of a catalytic amount of $PdCl_2(PhCN)_2$ with tin(II) chloride.

Allylic alcohols allylate various carbonyl compounds with regio-, chemo- and diastereo-selectivity in the presence of a catalytic amount of $PdCl_2(PhCN)_2$ and two equimolar amounts of tin(II) chloride.[1] Here we report that 2-methylenepropane-1,3-diol, bearing two identical allylic alcohol moieties, has been applied to (i) selective monoallylation, occasionally followed by cyclization to 2-substituted 4-methylenetetrahydrofurans, in DMF or THF and (ii) tandem diallylation of two different carbonyl compounds or 1,2-diones in 1,3-dimethylimidazolidin-2-one (DMI)–H_2O or THF–H_2O, using a Pd catalyst and tin(II) chloride.



2-Methylenepropane-1,3-diol **1a**†[2] was treated with benzaldehyde in the presence of $PdCl_2(PhCN)_2$ and $SnCl_2$ in DMF at room temperature and gave selectively the monoallylated 3-methylene-1-phenylbutane-1,4-diol (**2**; R^1 = Ph; R^2 = H, 73%), eqn. (1).‡ The results of the selective monoallylations of some aldehydes by **1a** are summarized in Table 1. The use of THF as a solvent lowered the monoallylation yield but enhanced the selectivity (entries 3 and 5). In contrast to diol **1a**, the palladium-catalysed reaction of 1,3-dichloro-2-methylenepropane (**1b**, 2 mmol) and benzaldehyde (1 mmol) with tin(II) chloride (2 mmol) did not produce the monoallylated product **2** but gave selectively the diallylated 1,5-diphenyl-3-methylenepentane-1,5-diol (**3**; R^1 = Ph, R^2 = H, 72 h, 92%) at room temperature in DMF. The reaction of **1a** (1 mmol) and benzaldehyde (2 mmol) with tin(II) chloride (4.2 mmol) at 50 °C in DMI–H_2O also led to selective diallylation (**3**; R^1 = Ph, R^2 = H, 15 h, 95%). Thus diol **1a** was applied to tandem carbonyl allylations with two different aldehydes; first carbonyl allylation with benzaldehyde at room temperature followed by a second carbonyl allylation with heptanal or 3-phenylpropanal at 50 °C, eqn. (2).

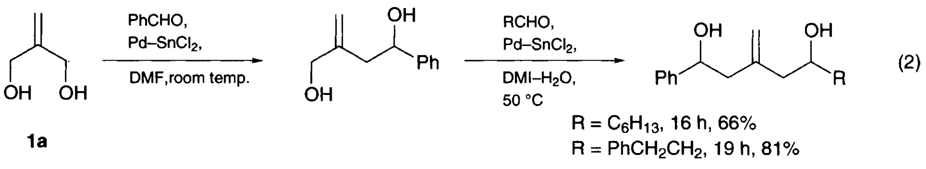
Table 1 Monoallylation of some aldehydes by **1a** with tin(II) chloride[a]

Entry	R^1	R^2	t/h	Yield[b] (%) 2	Yield[b] (%) 3
1	Ph	H	65	73	11
2	3,4-$(CH_2O_2)C_6H_3$	H	63	62	9
3[c]	4-$MeO_2CC_6H_4$	H	65	62	3
4	$PhCH_2CH_2$	H	42	57	9
5[c]	$PhCH_2CH_2$	H	116	51	0
6	C_6H_{13}	H	70	63	9
7	Ph	Me	90	27	0

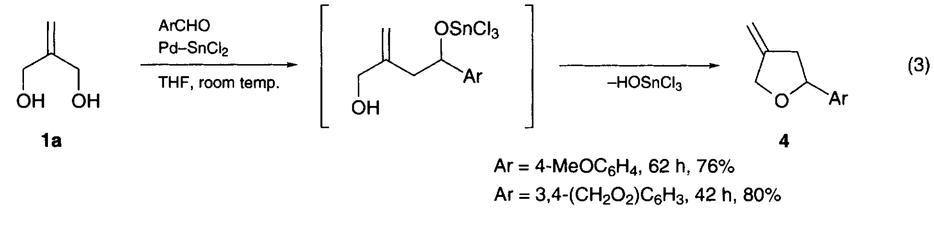
[a] Monoallylation of aldehydes (1 mmol) by **1a** (2 mmol) was carried out with $PdCl_2(PhCN)_2$ (0.02 mmol) and $SnCl_2$ (2 mmol) at room temp. in DMF (3 ml). [b] Isolated yields. [c] THF was used as a solvent.

Aromatic aldehydes bearing electron-donating groups such as 4-methoxybenzaldehyde and piperonal underwent the addition of **1a** with $PdCl_2(PhCN)_2$–$SnCl_2$ followed by intramolecular nucleophilic substitution (cyclization) at room temperature in THF to produce selectively 2-substituted 4-methylenetetrahydrofurans, eqn. (3). Aliphatic aldehydes and aromatic aldehydes bearing no electron-donating groups did not cause the cyclization even in THF; for example entries 3 and 5 in Table 1. The cyclization does not therefore seem to proceed *via* intramolecular nucleophilic attack of tin alkoxide to the π-allylpalladium formed from the second allylic alcohol moiety but *via* formation of a benzylic cation by the leaving trichlorotin oxide (Cl_3SnO) followed by intramolecular nucleophilic attack of allylic alcohol oxygen to its cation (S_N1-like).[3]

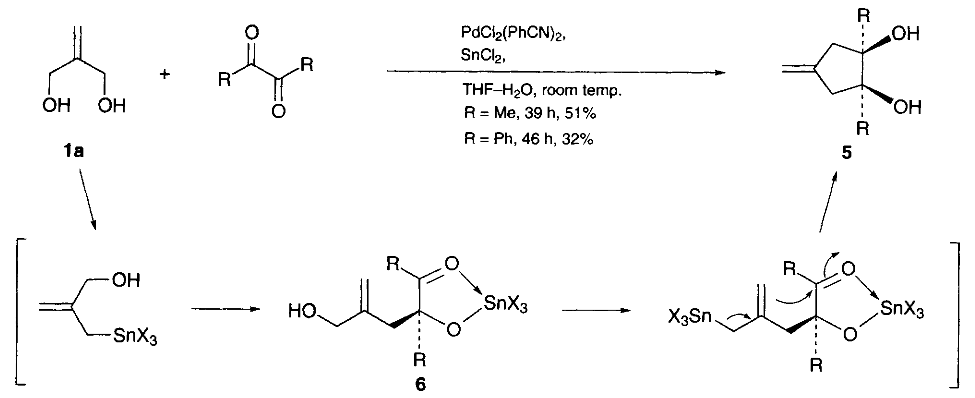
Intramolecular diallylation of 1,2-diketones by diol **1a** with $PdCl_2(PhCN)_2$–$SnCl_2$ was achieved in THF–H_2O at room temperature.[4] This reaction probably proceeds *via* formation of



R = C_6H_{13}, 16 h, 66%
R = $PhCH_2CH_2$, 19 h, 81%



Ar = 4-$MeOC_6H_4$, 62 h, 76%
Ar = 3,4-$(CH_2O_2)C_6H_3$, 42 h, 80%



(4)

activated 5-membered chelate intermediates **6**, similar to intermolecular diallylation of 1,2-diketones,[5] to produce only *cis*-4-methylenecyclopentane-1,2-diols **5**, as shown in eqn. (4).§ Dichloride **1b** cannot be efficiently utilized for intramolecular diallylation with benzil (40 °C, 40 h, 5%).

Footnotes

† 2-Methylenepropane-1,3-diol **1a** was prepared by the reaction of 1,3-dichloro-2-methylenepropane **1b** with calcium cabonate for 5 d in refluxing water; bp 125–126 °C/18 mmHg, 65%.

‡ *Typical procedure* for the monoallylation by **1a** with tin(II) chloride is as follows. To a solution of 2-methylenepropane-1,3-diol (**1a**, 0.18 g, 2 mmol), benzaldehyde (0.11 g, 1 mmol) and tin(II) chloride (0.38 g, 2 mmol) in DMF (3 ml) was added PdCl$_2$(PhCN)$_2$ (8 mg, 0.02 mmol). The solution was stirred for 65 h at room temp. under a nitrogen atmosphere and then poured into water (30 ml). The solution was then extracted with diethyl ether–dichloromethane (2 : 1, 120 ml). The extract was washed with water and then brine and then dried (anhyd. MgSO$_4$). Evaporation of solvents and purification by column chromatography (Merck silica gel 60 Art. 7734; hexane : ethyl acetate = 3 : 2) afforded 3-methylene-1-phenylbutane-1,4-diol (**2**; R^1 = Ph, R^2 = H, 0.13 g, 73%) and 1,5-diphenyl-3-methylenepentane-1,5-diol (**3**; R^1 = Ph, R^2 = H, 0.03 g, 11%).

§ In the diallylation of 1,2-diketones by 2-propen-1-ol with Pd–SnCl$_2$, the chelation of second carbonyl oxygen to tin in monoallylated trichlorotin alkoxide intermediates, formed by first carbonyl allylation of 1,2-diketones, has been found to promote the second carbonyl allylation and to control the diastereoselection; see ref. 5. Since intramolecular diallylation of 1,2-diketones by **1a** also proceeded at room temp. to produce only one diastereoisomer of 4-methylenecyclopentane-1,2-diols, the chelation of the second carbonyl oxygen to tin occurs and affords *cis*-isomers **5**. Neither monoallylated products **6** or *trans*-4-methylenecyclopentane-1,2-diols were detected by thin-layer chromatography. *Selected spectroscopic data* for *cis*-1,2-diphenyl-4-methylenecyclopentane-1,2-diol (**5**; R = Ph): ^{1}H NMR (JEOL GX-270, CDCl$_3$) δ 2.83 (dd, *J* 17, 1.7 Hz, 2 H), 3.21 (dd, *J* 17, 1.7 Hz, 2 H), 3.30 (s, 2 H), 5.13 (t, *J* 1.7 Hz, 2 H), 6.93–7.11 (m, 10 H).

References

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